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LIST OF ABBREVIATIONS

AAE	average absolute error
ABE	average bias error
AFDW	ash free dry weight
ARP	advanced radar plot
$CO_{2\text{-eq}}$	carbon dioxide equivalent
CP	center point
DG	digestate
DIN	Deutsches Institut für Normung
DM	dry mass
DOI	digital object identifier
EC	European Commission
ECO	economics
ENV	environment
G7	Group of Seven
GC	gas-phase chromatograph
GHG	greenhouse gas
GWP	global warming potential
HHV	higher heating value
HTC	hydrothermal carbonization
ICP-OES	inductively coupled plasma optical emission spectrometry
IKFT	Institut für Katalyseforschung und -technologie
ISO	International Organization for Standardization
KIT	Karlsruher Institut für Technologie
LCA	life cycle assessment
LCC	life cycle costing
LCSA	life cycle Sustainability assessment
MCBB	multi-criteria based benchmarking
MCDM	multi-criteria decision making
NAFTA	North American Free Trade Agreement
NASA	National Aeronautics and Space Administration
NPV	net present value
pH	potentia Hydrogenii
PROMETHEE	preference ranking organization method for enrichment of evaluations

ROE	return on equity
ROI	return on investment
SETAC	Society of Environmental Toxicology and Chemistry
SLCA	social life cycle assessment
SOC	society
TDA	technology design assessment
TRL	technology readiness level
UAF	unified appraisal framework
UNEP	United Nations Environmental Programme
UNFCCC	United Nations Framework Convention on Climate Change
US	United States
VDI	Verein Deutscher Ingenieure
VDMA	Verband Deutscher Maschinen- und Anlagenbau
WS	wheat straw

ABSTRACT

As part of the desired bio-economy, biomass will find a wide industrial application in the future, re-placing fossil resources and reducing the need of their import from insecure third countries. However, such an increased industrial application of biomass holds its own problems e.g. like an intensifying competition between food and fuel (and so an increasing competition for arable land) and sometimes other serious social problems, such as the so-called *Tortilla-Crisis* in Mexico in 2007. Therefore, (political) decision making within a bio-economy has not only to account for economic and ecologic aspects, but also for societal ones in the fields of human rights and justice. Moreover, the three aspects of sustainability (economics, environment, and societal aspects) are to be aligned and balanced within those decisions.

A standardized assessment methodology for biorefinery technologies, acknowledging all these aspects, has not been presented in literature so far. However, the need for such a standardized assessment framework was already discussed and demanded in the literature. In the present work, a basic architecture for such an assessment methodology as well as a standardized procedure for the selection of biorefinery technologies is presented (Section 2). The methodology includes thoroughly executed technology analysis by *Technology Design Assessments* (data level). It concerns explicit values and ethics by the use of the triple bottom line approach of sustainability on the impact level. On the decision making level a tailor-made multi-criteria decision making method (*Multi-criteria Based Benchmarking*) is proposed and *Advanced Radar Plots* are used for transparent and easy visual comparison of different policy options. The appraisal framework proposed goes beyond the literature on bioenergy appraisal frameworks and can be used as a baseline for future research.

Furthermore, first steps towards the implementation of the proposed methodology are undertaken. In this context, hydrothermal carbonization is used as an example as a promising

technology in a new developing bio-economy. Based on data from lab experiments, model equations are derived using a severity approach for proper mass balancing (Section 3 and 4). With these equations the product yields of hydrothermal carbonization (of biogas digestate and wheat straw) as well as the degree of carbonization of the hydrochar produced are quantified as functions of different process parameters using a severity approach. In contrast to other studies, a logarithmic dependence on process severity was applied. Process severity itself was calculated from temperature, retention time and catalyst concentration. By these models basing on few selected reaction conditions, a wide range of process conditions can be covered and the yields for the solid, liquid, and gaseous product phase can be predicted. The equations form the necessary data input for the basic *Technology Design Assessment* of HTC defined within the proposed standardized appraisal framework.

ZUSAMMENFASSUNG

Im Rahmen einer angestrebten Bioökonomie soll Biomasse in Zukunft wieder eine breite industrielle Anwendung finden und dabei fossile Rohstoffe ersetzen bzw. die Notwendigkeit ihres Importes aus unsicheren Drittstaaten reduzieren. Auf der Hand liegt jedoch, dass eine breite industrielle Anwendung von Biomasse eigene, z.T. schwerwiegende gesellschaftliche Probleme nach sich zieht. So kann die Verschärfung des Wettbewerbs zwischen Nahrungsmitteln und Treibstoffen (also die direkte Konkurrenz um Ackerland) gefährliche gesellschaftspolitische Folgen haben, wie die so genannte *Tortilla-Krise* in Mexiko im Jahre 2007 gezeigt hat. Die politische Entscheidungsfindung muss auf dem Weg zu einer Bioökonomie somit nicht nur ökonomische und ökologische Aspekte bei der Auswahl verschiedener Biomassekonversionstechnologien berücksichtigen, sondern auch gesellschaftliche Aspekte im Bereich der Menschenrechte und allgemeiner Gerechtigkeitsgrundsätze. Darüber hinaus sind Wirtschaftlichkeit, Umwelt, und Gesellschaft bei der Entscheidungsfindung miteinander in Einklang zu bringen.

Eine in diesem Zusammenhang standardisierte Bewertungsmethodik für zugehörige (politische) Entscheidungsprozesse, die all diese Aspekte berücksichtigt, fehlte bislang in der Literatur. Die Notwendigkeit eines solchen standardisierten Beurteilungsrahmens hingegen wurde in der Literatur jedoch bereits ausführlich diskutiert und eingefordert. Im Rahmen der vorliegenden Arbeit wird daher eine grundlegende Architektur für eine solche Beurteilungs- und Entscheidungsmethodik sowie ein dazugehöriges standardisiertes Vorgehen für die Auswahl von Bioraffinerie-Technologien in einer Bioökonomie vorgestellt (Sektion 2). Die Methode beinhaltet dabei die Beschreibung einer Prozedur zur Durchführung von Technologieanalysen (*Technologie Design Assessments* – Datenebene). Die Einbeziehung expliziter Werte und Ethik erfolgt dabei durch die Einbettung des so genannten *Triple-Bottom-Line* Ansatzes (auf der so genannten Einflussebene). Auf der Entscheidungsebene

kommt ein maßgeschneidertes multi-kriterielles Entscheidungsverfahren (*Multi-criteria Based Benchmarking*) zum Einsatz. Ferner werden hier so genannte *Advanced Radar Plots* eingesetzt, um einen einfachen und transparenten visuellen Vergleich verschiedener Entscheidungsoptionen zu ermöglichen. Der hier vorgeschlagene einheitliche Beurteilungsrahmen geht inhaltlich über die bislang in der Literatur diskutierten Ansätze hinaus und kann als Grundlage für zukünftige Forschungsarbeiten in diesem Bereich gesehen werden.

Über dies hinaus präsentiert die vorliegende Arbeit erste Schritte im Hinblick auf die Anwendung der vorgeschlagenen Bewertungsmethodik. In diesem Zusammenhang werden anhand von Daten aus Laborversuchen zur hydrothermalen Karbonisierung (als vielversprechende Beispieltechnologie für eine Bioökonomie) unter Berücksichtigung verschiedener Reaktionsintensitäten (*severity approach*), Modellgleichungen für die Massenbilanzierung abgeleitet (Sektion 3 und 4). Mit Hilfe dieser Gleichungen können die verschiedenen Produktausbeuten der hydrothermalen Karbonisierung (von Biogasgärresten und Weizenstroh), sowie der Grad der Karbonisierung der entstehenden Biokohle als Funktion von Prozessparametern berechnet werden. Im Gegensatz zu anderen Studien wurde hier eine logarithmische Abhängigkeit von der Reaktionsintensität verwendet. Letztere wurde dabei in Abhängigkeit von der Reaktionstemperatur, der Verweildauer und der Katalysatorkonzentration berechnet. Mit den ermittelten Modellen kann eine breite Palette verschiedener Prozessbedingungen simuliert und die Ausbeute der festen, flüssigen und gasförmigen Produktphase berechnet werden. Diese Modellgleichungen bilden die Grundlage für die Durchführung eines *Technology Design Assessments* als Ausgangspunkt für die Anwendung der vorgeschlagenen, standardisierten Bewertungsmethode.

SECTION 1

GENERAL INTRODUCTION

1. GENERAL INTRODUCTION

1.1 Introduction

The use of solar energy stored in biomass for food, feed, and fuel has long tradition in human history [1] and has played an essential role in the industrialization of the modern world in the beginning of the 19th century [2, 3]. From the middle of the 19th century on, man learned *"to tap the ancient solar energy stored in coal, oil, and natural gas"* [4]. This catalyzed industrialization and improved human living standards considerably. Since then the availability of cheap crude oil has been the precondition for steady economic growth and an increasing human world population [5, 6]. More than 95 % of all industrial goods manufactured are directly or indirectly dependent on the availability of low-cost petroleum. Oil is the most important primary resource for the production of fuels, drugs, dyestuffs, and drapery today [7].

However, oil is a finite resource and there is an ongoing discussion about the appearance of *Peak Oil* in literature [8–11]. Peak oil does not mark the end of the oil-age, but (theoretically) rather the point in time on which the worlds' oil production (e.g. supply in barrels per day) reaches its overall maximum and the price for crude oil increases continuously (apart from short-term economic fluctuations). This effect results from the increasing depletion of the known conventional oil reserves and the steadily increasing demand [4, 12]. Although there is a controversy among scientists about the exact appearance of peak oil, it is commonly acknowledged that peak oil will happen sooner or later. A first summary of different estimates on its appearance has been given early by Hirsch et al. [13]. Estimates found by the authors range from 2010 (and earlier) [14] to 2025 [15]. More recent publications estimate peak oil to appear in 2015 [10], in 2028 [11], or between 2009 and 2021 (depending on what kind of depletion scenario for conventional crude oil is chosen) [9, 16].

In contrast, Murray and King assume that peak oil already happened, because they observed that *conventional* crude oil production has not risen since 2005. The authors used a scatter plot and revealed a price inelastic crude oil production with data based on years from 2005 to 2011 (see red-x data cloud in Fig. 1.1). Further, they compared data from the years 1998-2004 (grey-circles data cloud in Fig 1.1) and showed that crude oil production has been rather price elastic within these years, bearing a peak in production at round about 75 million barrel per day. Therefore, the authors assumed that the maximum production level for conventional crude oil has already passed , meaning that the oil market already entered into a phase of transition since 2005 [6].

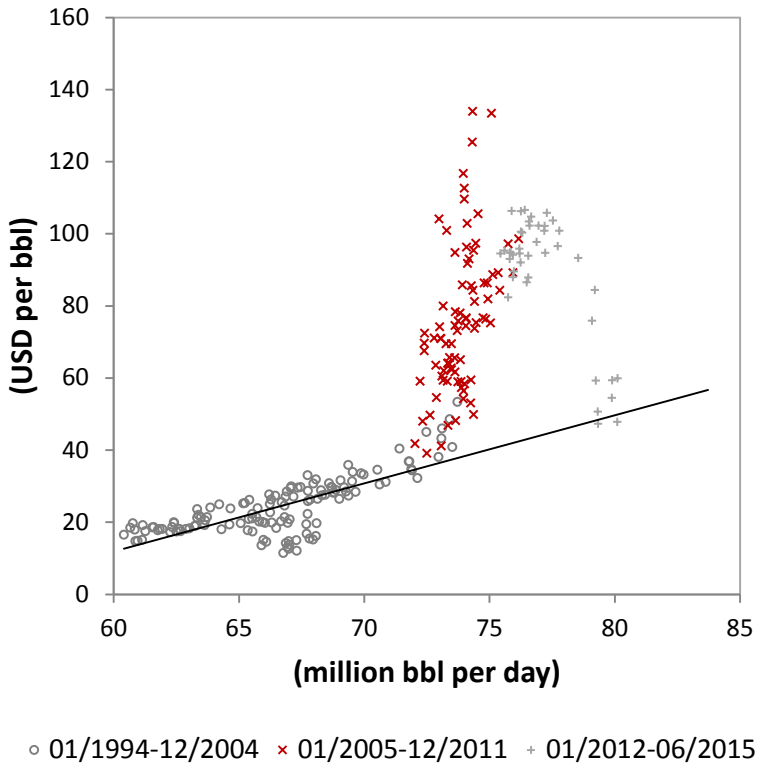

Fig. 1.1: Crude oil production versus crude oil price – A scatter plot on price elasticity for three different periods (Data Source: US Energy Information Administration – 12/2015).

Fig. 1.1 shows a similar scatter plot created from updated average monthly data from the US Energy Information Administration (1994 - mid 2015). This data shows, that the pattern identified by Murray and King today still is more or less the same. Looking specifically at the post 2011 (grey-cross data cloud) period, it can be seen, that the peak in production was

extended to more or less 80 million barrel per day, causing price deterioration in combination with a weak crude oil demand due to a weak world economy today. However, looking at the very detail of the post 2011 production data reveals, that almost all of the additional 5 million barrel crude oil production (per day) today stems from the depletion of unconventional sources (e.g. like oil shale) in North America, namely in the US which started in the end of 2011 and increased sharply since then. In respect to this, the peak of conventional crude oil production still seems to exist at round about 75 million barrels per day.

Concerning this, in recent years almost all G7 countries (as well as the European Union, except Italy) established policies to foster the transformation of the existing oil-based economy into a bio-based economy (bio-economy) within the next decades [17]. It seems that energy and resource insecurity resulting from peak oil is more threatening to politicians and therefore more relevant to foster political action compared to the threat of climate change [6]. In this respect, broad future industrial application of biomass is assumed to substitute depleted fossil feedstocks and to reduce imports of fossil resources [18]. However, it should be clear, that an increased industrial application of biomass brings its own problems, e.g. like intensifying competition between *food and fuel* and all social impacts associated [19, 20]. Subsequently, the next section focuses on the problems connected with a re-increasing use of biomass for non-food purposes.

1.2 Impacts associated with the non-food use of biomass

Today, there is consent that an intensifying use of biomass for non-food purposes is capable of shifting environmental problems to other world regions and provoking social impacts in these regions respectively [19, 20]. The underlying basic problems are an increased competition for arable land for food and non-food purposes (stemming from an increased demand for energy), while petro-chemical resources become less available [4] and more volatile in prices [21]. As mentioned earlier, almost all G7 countries (as well as the European Union) have set-up strategies to foster the transition to a bio-economy [17]. Taking this into

account, it has been estimated, that the available agricultural area in Europe for food production will decrease by 3 to 8 % until 2040. Although agricultural productivity is assumed to increase within the same timeframe [22], the detention of land to serve other demands than food production is leading to an intensifying worldwide competition for arable land [23–25]. As a result, pressure on land conversion increases, aggravating climate change (e.g. when savannas, peat lands, and rainforests are converted to agricultural land) [23, 26].Other socio-economic aspects, e.g. like free trade agreements between developed and newly industrializing countries can further intensify such competition and lead to political unrest in the countries affected.

A prominent example for such a catalyzing effect is the *Tortilla Crisis* in Mexico [27] where the North American Free Trade Agreement (NAFTA) led to the removal of import tariffs on maize in Mexico and made the country dependent on cheap US maize imports. While at the beginning of NAFTA in 1994 this was a blessing to the countries basic food supply, the situation changed when the *US Ethanol Programme* was launched. The use of ethanol from US maize as a fuel was supposed to reduce GHG emissions by 20 % compared to petrol [28][1]. Subsequently, financial incentives from the programme shifted major parts of the US maize production from export to domestic ethanol processing. Import prices for maize increased in Mexico and made the price for tortillas (the most elemental food in Mexico) rise by 69 % between 2005 and 2012 [29]. It was found that this led to reduction of Mexican household living standards between 2006 and 2008. The poorest Mexicans were most affected as their spending on tortillas increased significantly compared to total income [30]. Political unrest was the direct impact in 2007. Further, there is statistical evidence for biofuel production and crude oil price having a significant effect on increasing food prices [31]. The underlying

[1] Although there is a reduction of GHG emissions by the use of ethanol from US corn, this achievement is weak compared to GHG reduction by ethanol from Brazilian sugarcane (85 %) or Swedish wheat (80%) [28].

conflict between food, energy and the environment has previously been called the '*trilemma challenge of bioenergy'* [21].

In terms of the "right" bioenergy system to be applied, the trilemma challenge reveals, that decision making within a bio-economy has not only to account for economic and ecologic aspects, but also for societal ones in the field of human rights, stewardship and justice [32]. At the same time the economic, environmental, and societal dimension constitute the concept of sustainability in the so called '*triple bottom line approach*' [33-35]. A standardized methodology for assessing biorefinery systems therefore needs to integrate these three dimensions. In this respect, the need for a unified appraisal framework (UAF) has been stressed extensively in literature [35–38]. It was emphasized that a working UAF can essentially improve bioenergy policymaking by offering a structured and transparent approach to resolve the *bioenergy trilemma* and to identify, whether a certain biomass conversion technology should be implemented or not. Being able to better investigate and transparently show the interdependencies between economy, environment and society [36, 39], existing and future policies could be improved [35].

1.2.1 Critical review of approaches for the assessment of biomass conversions systems

After reviewing extensive literature and setting up a formal definition for an integrated appraisal approach, Boucher et al. [38] selected 20 out of more than 1,300 publications sources (publication dates are ending in 2011) that already came close to a UAF. The authors defined UAFs are *"strategies and/or standardized procedures for gathering, prioritising and communicating information about biofuels, involving analysis and judgement, and meant to support decision-making or policy forming".* Within their appraisal it was assessed to which extent the selected key assessment reports addressed impartiality, transparency, participation (of lay people, experts and stakeholders), scientific evidence basis, focus on uncertainties, and explicit values and ethics.

A rating/scoring system was applied by assigning values from 1 (absence of discussion/engagement) to 5 (substantive discussion/priority engagement) to the characteristics mentioned above for each report. Impartiality, scientific evidence basis, and transparency are the most important appraisal properties applied. However, participation of lay people and stakeholders as well as the use of explicit values and ethics in the decision process are weak in almost all key assessment reports. The authors recommend focusing less on the details of the single building-blocks of a UAF but rather on the question how existing methods and knowledge can be better aligned in further research [38].

After the review of Boucher et al. (ending in 2011), an additional literature review on biofuels assessments was executed. Between 2011 and 2014 several relevant assessment papers from peer-reviewed journals can be identified [40–47]. However, only a few of them are combining the triple bottom line with a standardized procedure for strategic decision making and policy support, namely Santoyo-Castelazo and Azapagic [40], Diaz-Chavez [44], Fontanta et al. [42], and Gnansounou [45].

Gnansounou [45] present a logic-based model for the sustainability assessment of biofuels by a hierarchical structure to connect specific sustainability indicators with more general ones. The strengths of this approach are its transparency and simplicity. However, its hierarchical structure forms its main weakness by implying independency of the different indicators used. Fontana et al. [42] present a systematic framework that includes the ecosystem services as criteria into a *multi-criteria decision making (MCDM)* approach. Using the central Alps as the region of investigation, the authors compare three land-use alternatives resulting from land-use change caused by socio-economic pressures. The advantage of this approach is its inherent flexibility and the integration of explicit values and ethics. However, the use of the software PROMOTHEE makes the procedure less transparent and the exclusion of lay people throughout the weighting procedure ignores an essential requirement from literature [38].

Diaz-Chavez [44] proposes an appraisal framework based on matured environmental management tools for data gathering as well as the triple bottom line, which is extended to a fourth dimension, namely “policy and institutions”. The advantages of this approach are its scientific base, inclusion of explicit values and ethics as well as the triple bottom line. However, this approach lacks a definition of a weighting procedure for single sustainability categories and criteria. Furthermore, a procedure for data aggregation with regard to decision making is missing. Finally, “policy and institutions” are an inherent part of the societal dimension of sustainability and should, therefore, not be separated from it.

Santoyo-Castelazo and Azapagic [40] present a decision-support framework for energy systems in general that integrates the triple bottom line and combines decision making data with a MCDM approach. The authors apply this appraisal framework to the electricity system of Mexico. This approach seems to be the most elaborated appraisal framework in the context of energy system assessments. However, the authors neither define guidelines for data gathering, category and criteria selection, nor a procedure for the weighting of the sustainability indicators used. Moreover, sustainability criteria are subjectively preselected and the approach lacks transparency due to a missing description of the data processing methods and a missing visualization procedure for the results from MCDM.

1.2.2 Special challenges in assessing new (future) technologies

An important prerequisite for the assessment of technological systems with respect to biomass conversion is the availability of substantial quantitative data about mass and energy balances. This is required for proper design of a process flow chart and reliable thermodynamic calculation. One way to gather such data is through an extensive review of existing literature. Such a review might generate all data needed, especially with regards to matured or popular biomass conversion technologies. However, for premature technologies (such as Hydrothermal Carbonization), conclusive and reliable data will probably not be found in

literature. In this case, data must be gathered by conducting own experimental research. Obviously, such a step must be part of a standardized assessment methodology as well. The credibility of the assessment results within all three dimensions of sustainability will be dependent on such a step.

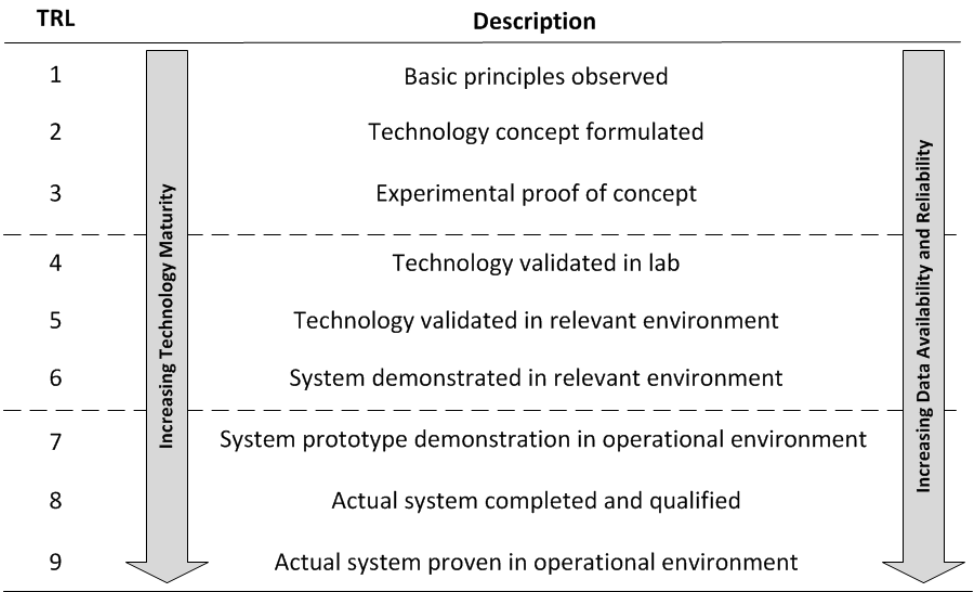

Fig. 1.2: Technology Readiness Level adaption by the European Commission [51].

Further, by assessing new technologies it is likely that technologies with distinct levels of maturity are to be compared. Thus, the maturity level of distinct technologies should be classified. The concept of the *Technology Readiness Level (TRL)* after Mankins [48–50] might be very useful in this respect. TRL is a "*systematic metric/measurement system that supports (technology) assessments of the maturity and the consistent comparison of maturity between different types of technology*" [48]. It has been developed by NASA in the 1970s and became part of a NASA management instruction (NMI 7100) in the 1990s. After this, it was adapted by several US and international institutions, e.g. the European Commission (EC), to better be able to measure and compare technology maturities in different contexts [49].

Fig. 1.2 shows the TRL classification adapted by the EC and the meaning of the different levels used for instance in EC calls for research proposals. Besides providing information

about maturity, the TRL can also indicate the reliability of the data used for the assessment of a biomass conversion system.

1.3 Biomass conversion technologies vs. biomass conversion systems

The term *'biomass conversion technology'* means a single process or technical method to upgrade biomass to fuels or other chemical products with higher value [52–54]. Contrary to this the term *'biomass conversion system'* is not clearly defined in literature. Within the work at hand a biomass conversion system (or also biorefinery system) is defined as contemplation of at least more than two steps of the bio-based value chain. For example, in a Cradle-to-Gate approach a biomass conversion system would consist of technologies used for biomass cultivation, transport and storage, and then for the production of primary products (e.g. solid, gaseous, and liquid intermediates - compare Fig. 1.3) [52]. For the assessment of biomass conversion technologies the extension to the system level is critical as the upstream biomass cultivation and extraction looms large in the environmental, economic and societal assessment (see also section 1.2) [55].

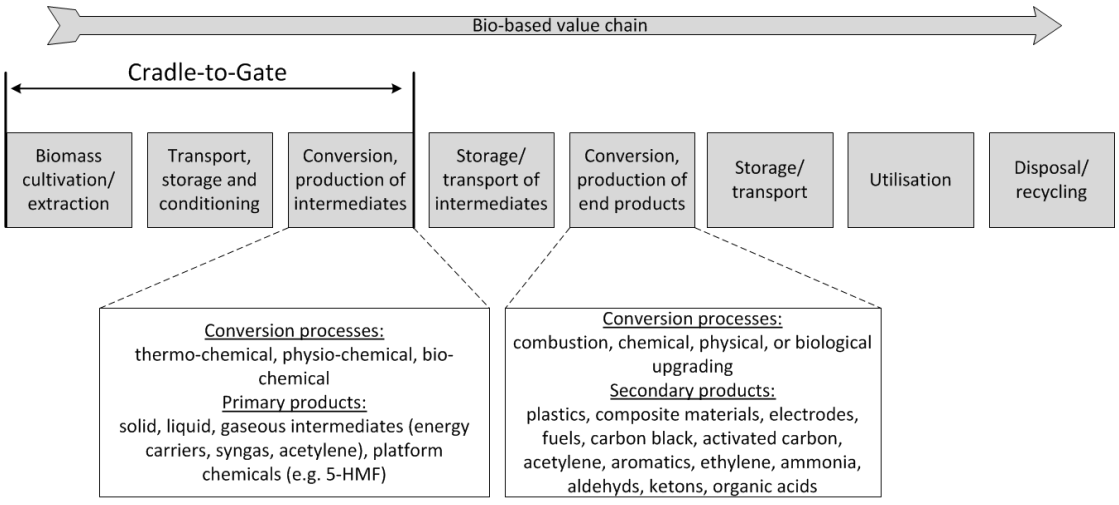

Fig. 1.3: Bio-based value chain, biomass conversion systems, biomass conversion technologies and possible primary and secondary products from biomass conversion.

1.3.1 Biomass conversion technologies and routes

Biomass conversion technologies are typically classified in physicochemical, bio-chemical, and thermo-chemical conversion routes for the production of primary products namely

intermediates, fuels, and platform chemicals (see also Fig. 1.3). The physicochemical conversion route means the extraction of bio-oil from oil seeds and the transesterification thereafter for the production of biodiesel. The bio-chemical conversion route refers to the production of bio-ethanol by alcoholic fermentation, biogas production by anaerobic digestion, and compost production by aerobic fermentation [56].Within the thermo-chemical conversion route gasification, liquefaction, carbonization as well as direct combustion technologies can be distinguished [53]. Regarding thermo-chemical biomass conversion technologies, for an optimal conversion the biomass needs to be dried to water contents below 10 wt.-% [57].

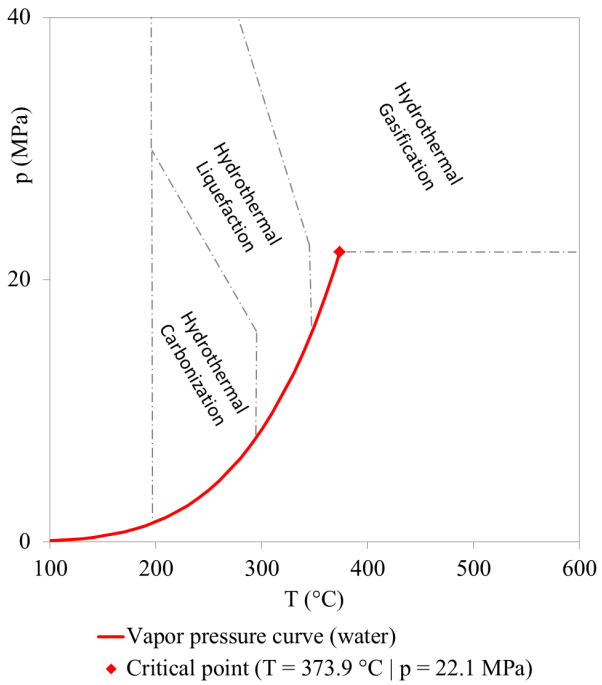

Fig. 1.4: Reaction conditions (schematic) of different hydrothermal conversion technologies and the vapor pressure curve of water.

In contrast, the hydrothermal thermo-chemical conversion technologies do not require such a pretreatment. Within the hydrothermal conversion route, wet biomass (70 wt.-% water content or more) can directly be converted into fuels and platform chemicals without prior and energy-intense drying [58]. Hydrothermal conversion takes place in close association to the vapor pressure curve of water. Within hydrothermal processes, pressure needs to steadily maintained above the occurring vapor pressure so that the water (as a solvent for

intermediates and also as a reactant) stays liquid throughout the whole reaction procedure. In this respect, the critical point at the end of the vapor pressure curve does not mark a limit for hydrothermal biomass conversion. Hydrothermal reactions also take place when the water reaches a super-critical state [57, 58]. Fig 1.3 gives a schematic overview about reaction conditions of different hydrothermal conversion technologies and their relation to the vapor pressure curve of water.

1.3.2 State of the art in hydrothermal carbonization

Among wet thermo-chemical technologies for biomass conversion, hydrothermal carbonization appears to be a promising technology due to high advances in recent research. The term hydrothermal carbonization (HTC) describes the treatment of wet biomass with hot, pressurized water to produce a lignite-like solid hydrochar [59–61]. The essential functioning of the process has already been discovered at the beginning of the 20th century by Bergius [62], but the commercial use at large scale becomes relevant just by today due to an increasing scarcity of fossil resources [59].

The HTC technology mimics the natural, millions of years lasting, geological process of coal formation [63]. It occurs within several hours (1-72 hours) and at relatively low temperatures (200-300 ° C) and pressures [57, 61, 64]. As a thermo-chemical process, HTC is capable of especially converting wet biomass into a homogeneous carbon-rich solid (hydrochar) [60, 65]. Throughout the reaction gas is formed, increasing the pressure above the vapor pressure of water inside the reaction containment. Thus, the water remains liquid even at temperatures above 100 ° C [61]. In addition to the homogeneous distribution of heat in the reaction chamber preventing local overheating, water also serves as a solvent and reactant for intermediate products. In order to eliminate char and coke, the biomass must be completely covered with water during the entire reaction period. The occurring main reactions are hydrolysis, dehydration and decarboxylation as well as polymerization by condensation [66].

Due to their complexity and interaction of different reaction pathways the exact reaction pathways are today still investigated. Only for pure substances such as lignin, cellulose and glucose they are well understood [59, 65]. The overall reaction takes place under release of energy (exothermic) and requires certain activation energy for initiation [60, 61, 67]. In terms of mass balancing and product yield estimation of the process only little work has been done so far. Li et al. [68] collected HTC data from literature and used multiple linear regression models to predict yields (solid, carbon content, energy content and C content in different product phases) for different process conditions.

A significant advantage of HTC technology in comparison to other thermo-chemical biomass conversion processes is that the biomass does not need to be dried energy-intensively prior to conversion [57, 64]. The water contained in the biomass is an important reaction medium within the process. After the conversion, the HTC product can be separated from the water by simple mechanical methods (for example pressing) and with little energy input due to the changes in physical and chemical material properties [57, 69, 70]. Because of this, the range of biomass feedstocks for the HTC process is wide, ranging from waste materials from the food industry, sewage sludge [71–73] to agricultural side-products [74–94]. The use of energy crops is also conceivable. However, their use is not desirable due to the trilemma challenge of bioenergy (see section 1.2) and its ongoing debate on sustainable land use [85, 92, 94–99].

The hydrochar produced by HTC is similar to lignite in terms of its heating value. The actual product quality can be controlled by varying the process parameters namely process temperature, retention time, and reaction pressure, nature of the biomass in terms of water content, particle size, lignin content, and pH in the initial suspension [82, 100]. The range of possible applications for the hydrochar is large (see Fig. 1.5). The hydrochar can directly be utilized as a soil conditioner [80, 93, 94, 96, 101, 102], fuel [77, 91, 103, 104], carrier medium for catalysts, ion exchanger and as activated carbon for the purification of waste water and

off-gases [64, 86, 88, 105–110]. Moreover, it is conceivable to produce carbon black and high-quality electrodes as well as composite materials [86, 88, 105–110]. In addition to the direct use, also the classical pathways developed for fossil fuels for the production of platform chemicals can be applied. The successful operation of a pilot plant for the production of high-purity syngas based on hydrochar from HTC has already been demonstrated [111]. Additionally the use path through the production of calcium carbide and corresponding acetylene chemistry are discussed [112].

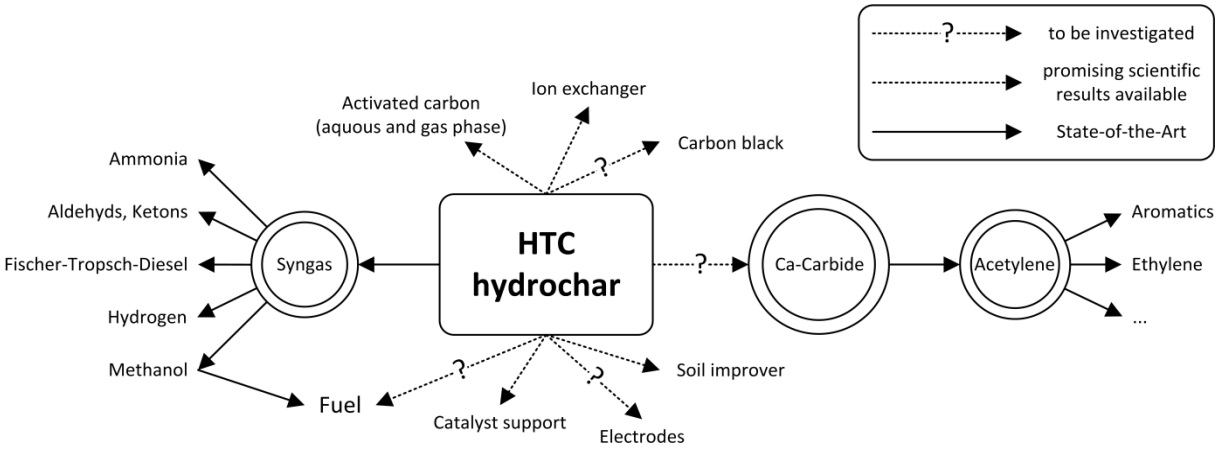

Fig. 1.5: Possible applications of HTC hydrochar and their state-of-the-art [112].

Currently, different reactor concepts are developed and tested for the commercial implementation of the HTC technology. Research devotes special attention to continuously working tube reactors as well as on semi-continuous batch processes. Heat recovery and waste water treatment concepts have to be part of the plant concept [59, 64, 69, 113]. The waste water from HTC itself is heavily charged with organic carbon and suitable for re-use in biogas production [79, 114] or as a nutrient for growing microalgae, because of the inorganic content [115–117].

1.4 Conclusions

1.4.1 Assessment of biomass conversions systems

It has been shown, that a UAF for biomass conversion systems that addresses all relevant aspects demanded in literature, has not been presented so far. Such an overall assessment

methodology should better integrate existing knowledge and methodologies [38] to improve decision making in a bio-economy and be able to enhance and compare the impact and the overall value of specific technologies within a bio-based value chain [35, 36]. Such an approach should be impartial, transparent, and should improve the integration of uncertainties. Furthermore, it should involve lay people, experts and stakeholders, and better address explicit values and ethics [38]. To better tackle the bioenergy trilemma, it should also integrate the three dimensions of the triple bottom line approach of sustainability and provide rudimental instructions for data gathering and analysis.

1.4.2 Hydrothermal Carbonization

A lot of valuable research has been done on HTC in recent years. Although also some effort has been done to set-up statistical models for the prediction of the solid mass yield and the energy content of HTC hydrochar [68], the accuracy of the model equations found is low ($B_{cor} \leq 0.79$), limiting the practical usability of the approach proposed in the literature. Moreover, the models do not cover the influence of a catalyst on the outcome of the process and are lacking the description of a complete process mass balance in terms of gas yield and liquids. Further, applicability of the models for common agricultural side products like biogas digestate or wheat straw - both broadly available and interesting feedstocks in Germany – is uncertain. So far, highly accurate and complete models for mass balancing are missing for these feedstocks, despite their high relevance for a proper assessment of the HTC technology within a UAF.

1.4.3 Research objectives

Based on the analysis the following research objectives are inferred:

a. Development of a unified appraisal framework for biomass conversion systems addressing the bioenergy trilemma by integrating the triple bottom line of sustainability as well as all other demands emphasized in literature.

b. Development of accurate statistical models for the prediction of product phase yields and hydrochar quality of HTC of different biomass based on data gathered by lab experiments with the aim to properly apply the UAF proposed.

1.4.4 Structure of the thesis

This cumulative dissertation is composed of three articles, all published in peer-reviewed journals. Sections 2-4 represent one publication each. References can be found at the end of each section. Reprints were made with permission from the respective publishers. Fig. 1.6 depicts the interplay of all publications presented in the work at hand graphically.

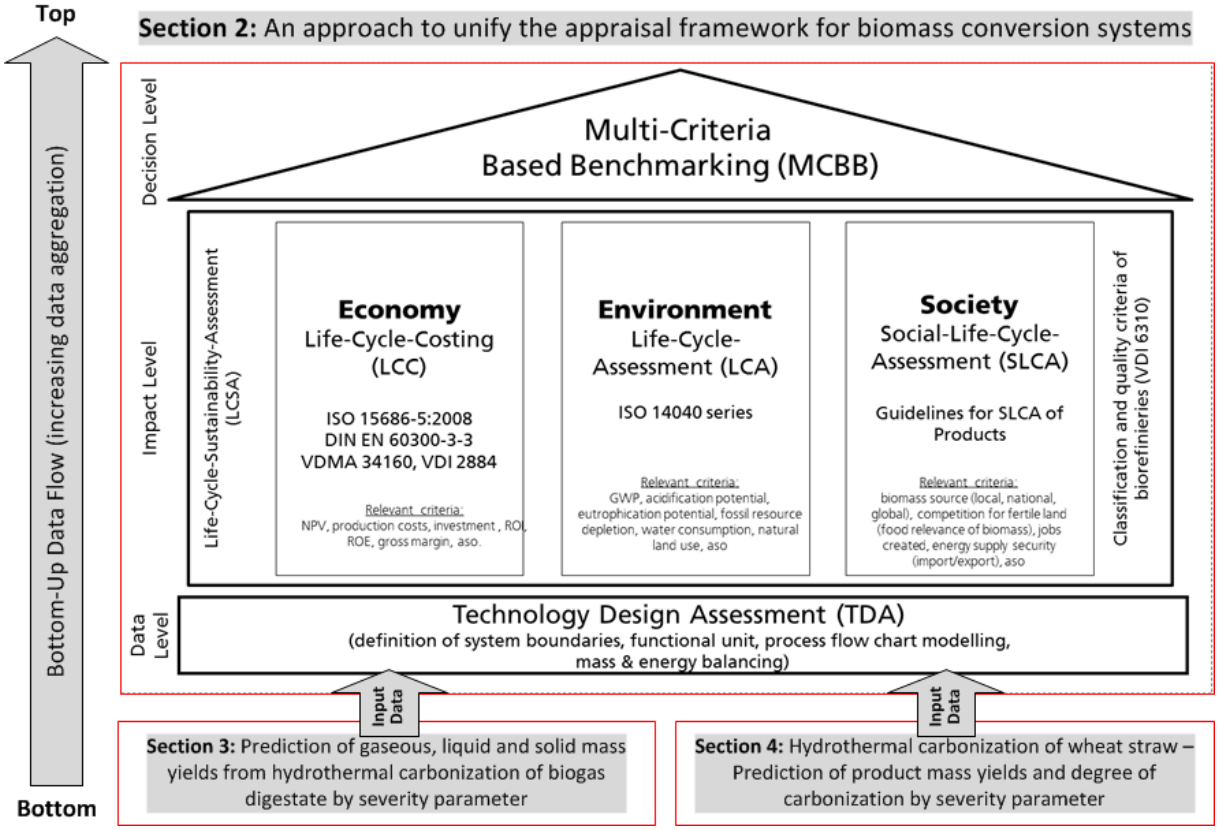

Fig. 1.6: Interplay and connection of the research papers presented in Section 2-4.

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SECTION 2

AN APPROACH TO UNIFY THE APPRAISAL FRAMEWORK FOR BIOMASS CONVERSION SYSTEMS[2]

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2. AN APPROACH TO UNIFY THE APPRAISAL FRAMEWORK FOR BIOMASS CONVERSION SYSTEMS

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Abstract

The need for a unified appraisal framework for biomass and bioenergy has been extensively discussed in literature. It is emphasized that a working unified appraisal framework can essentially improve bioenergy policymaking by offering a structured and transparent approach to tackle the *bioenergy trilemma* and to work out whether or not a certain biomass conversion technology or system should be implemented (always in direct comparison to others). Further, such an approach could be used to better examine the interdependencies of the single elements of the *triple bottom line of sustainability* (economy, environment, society). This also would lead to the improvement of existing and future policies and would give bioenergy a better foundation within the ethical debate by transparently showing the trade-offs between economy, environment and society. This paper drafts a unified appraisal framework for biomass conversion systems that integrates different approaches on the data, impact and decision making level. On the bottom line the proposed architecture in total addresses all relevant requirements from literature and fits well into the valuable work that has been done previously.

Keywords

unified appraisal framework, sustainability assessment, biomass, biofuels, advanced radar plots, multi-criteria decision making

2.1 Introduction

The need for a unified appraisal framework (UAF) for biomass and bioenergy has been extensively discussed in literature [1–4]. It is emphasized that a working UAF can essentially improve bioenergy policymaking by offering a structured and transparent approach to tackle the bioenergy trilemma [5] and to work out whether or not a certain biomass conversion technology or system should be implemented (always in direct comparison to others). Further, such an approach could be used to better examine the interdependencies of the single elements of the triple bottom line of sustainability (economy, environment, society) [4]. This also would lead to the improvement of existing and future policies and would give bioenergy a better foundation within the ethical debate by transparently showing the trade-offs between economy, environment and society [1, 6].

It has been shown that in recent years numerous appraisals of biomass conversion systems have been done to progress this task [3]. Liew et al. [2] discovered that within these tries a typical process pattern is applied regularly. This pattern starts with the evaluation and modelling of the technical background of the technologies or value chains on scope (data level), which is followed by an impact assessment by relevant tools (impact level – based e.g. on the triple bottom line approach), and closed by the application of a scoring model (almost Multi-criteria Decision Making approaches) to rank the relevant alternatives (decision making level).

Within an extensive literature review Boucher et al. [3] selected 20 key assessment reports out of more 1,300 sources that already came close to an UAF. They defined that UAFs are formulated as *"strategies and/or standardized procedures for gathering, prioritising and communicating information about biofuels, involving analysis and judgement, and meant to support decision-making or policy forming"*. It was assessed to which extend the selected key assessment reports addressed impartiality, transparency, participation (of lay people, experts and stakeholders), and scientific evidence basis, focus on uncertainties, and explicit values

and ethics. It was found that especially impartiality, scientific evidence basis and transparency were the most important appraisal properties applied. However, participation of lay people and stakeholders as well as the embedment of explicit values and ethics in the decision process was found to be weak for almost all of them. The authors recommended focusing less on the details of the single building-blocks of a UAF but rather on how existing methods and knowledge can better be integrated for further research [3].

For the years following the review of Boucher et al. (which ends in 2011) a number of relevant assessment papers from peer-reviewed journals can be identified [7–14]. Only a few of them are really combining the triple bottom line with a standardized procedure for strategic decision making and policy support. In this regard the works of Santoyo-Castelazo and Azapagic [7], Diaz-Chavez [11], Fontanta et al. [9], and Gnansounou [12] are specially worth noting.

Gnansounou [12] presented a logic-based model for the sustainability assessment of biofuels by a hierarchical structure. The strengths of the approach presented are intrinsic transparency and simplicity. However, its hierarchical structure forms the main weakness which implies independency of the different indicators. Fontana et al. [9] presented a systematic framework that included the ecosystem services as criteria into a multi-criteria decision making (MCDM) approach. The advantage of this approach is its flexibility and the involvement of explicit values and ethics. However, the use of the software PROMOTHEE makes the procedure less transparent and lay people are also excluded from the weighting procedure [3]. Diaz-Chavez [11] proposed an appraisal framework based on matured environmental management tools for data gathering as well as on the triple bottom line. The approach is scientific evidence based, includes explicit values and ethics and also the triple bottom line. However, it leaves out to define a weighting procedure as well as a procedure for data aggregation with respect to decision making.

Santoyo-Castelazo and Azapagic [7] presented a decision-support framework for energy systems in general that integrates the triple bottom line and aggregates decision making data with a MCDM approach. Although this approach seems to be the most elaborate integrated appraisal framework in the context of energy system assessments, it does whether define guidelines for data gathering, category and criteria selection, nor a procedure for the weighting of the sustainability indicators used. Moreover, criteria are preselected and the approach is lacking in transparency due to a missing description of the data processing methods and a visualisation procedure.

Considering these findings, this paper drafts a UAF for biomass conversion systems that integrates different approaches on the data, impact and decision making level. On the bottom line the proposed architecture in total addresses all relevant requirements from literature and fits well into the valuable work that has been done previously.

2.2 Material and methods

The following sections describe the architecture of the UAF. Although the approach can be adapted for any other decision problem, the scope of this work is the assessment of biomass conversion systems, for which it specifically has been developed. The approach relies on data input (foundation – data level) that is fed into a tripartite assessment process (pillars – impact level), covering economic, environmental and societal aspects. Results of the assessments are integrated and evaluated through the use of an appropriate Multi-criteria decision making (MCDM) methodology (rooftop – decision level, compare Fig. 2.1).

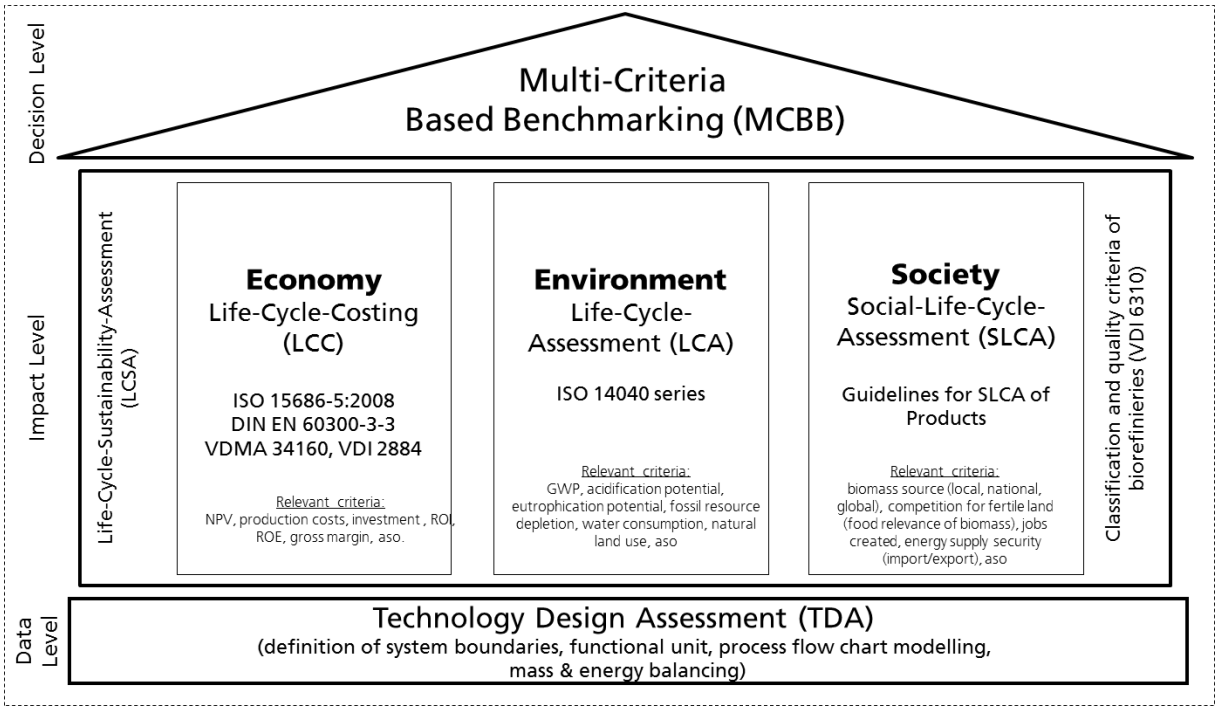

Fig. 2.1: The architecture of the UAF is based on a combination of matured methods, tools and norms and a tailor-made MCDM method called Multi-Criteria Based Benchmarking.

2.2.1 Technology Design Assessment – the data level

A review of the literature on bioenergy systems assessment [15–22] shows that technical criteria are often directly incorporated into the assessment of bioenergy conversion systems and treated equally to other assessment criteria e.g. from the triple bottom line. Such an approach can easily introduce a bias towards technological properties, since most criteria found within the triple bottom line are proxies for basic technical criteria (e.g. like energy efficiency, reliability and maturity). To avoid such double counts, our UAF is built-up differently.

As depicted in Fig. 2.1, the UAF is in its first step based on a comprehensive technological assessment called Technology Design Assessment (TDA). The basic assumption is that nearly all economic, environmental, and societal impacts of a technology can directly be derived from the physical and technical properties of the involved technologies within the value chain. For that reason, the TDA includes the definition of the system boundary (Fig. 2.2) and the corresponding cut-off criteria, the definition of the functional unit (e.g. MJ of produced energy or Mg of used biomass) to be assessed, the modeling of a process flow chart for all

phases of the conversion system and detailed mass and energy balancing for all phases of the value chain on scope. A good example for comprehensive mass and energy balancing can be found in literature [23].

Especially for biomass conversion systems, the upstream biomass cultivation and extraction looms large in the environmental, economic and societal assessment. The system boundaries of the TDA therefore include the agricultural processes or the processes related to biomass extraction, biomass transport and storage as well as the biomass conversion in a biorefinery itself [24]. The use of cradle-to-gate approaches as standardized system boundaries is therefore recommended in the UAF. 'Gate' here means the exit gate of the biorefinery. Depending on what kinds of products are assessed there could be two different definitions of the exit gates of relevance. When just energy carriers e.g. biogases, bio-crudes, solids or platform chemicals are produced, the gate definition differs from a production process where end energy, chemicals or raw materials are provided. Fig. 2.2 depicts the difference between these two gate definitions. For the TDA an appropriate gate definition needs to be selected. However, in some cases the recommendation above might be too narrow (e.g. in the case of liquid and solid biofuels), so that in such a case the whole life cycle from cradle to grave needs to be evaluated.

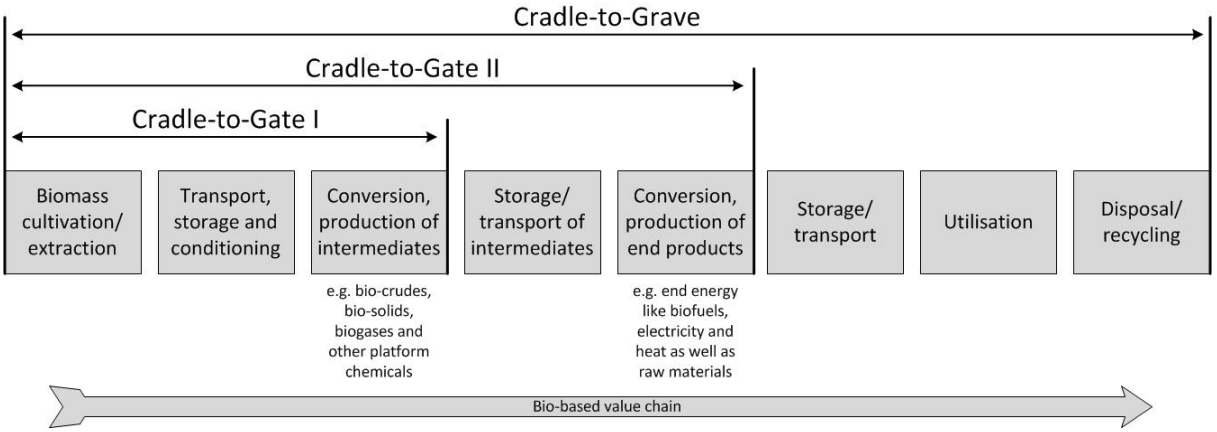

Fig. 2.2: Definitions of possible system boundaries for biomass conversion systems.

Especially for new biomass conversion systems, for which data is scarce, it is required to produce custom data by lab experiments and thermo-dynamical calculation for a reliable execution of the TDA. For more matured technologies it is very likely that corresponding data can be found in the literature. In order to increase data comparability, especially between matured biomass domains and newly developing ones, two different approaches can be used. The first and less labor-intensive one is to use the structure of available data on existing biomass domains as a template for data production for newly developing ones. However, this approach limits future biomass system development and innovation. It should only be used when the system boundaries for both are well-aligned. The second approach is more labor-intensive, requiring the development of a common data structure for emerging as well as established biomass domains. While this implies that data sets for established biomass conversion systems need to be produced anew, it would allow for future system comparisons to be more accurate and reliable.

2.2.2 Life-Cycle-Sustainability-Assessment – the impact level

The connection between the TDAs and the MCDM step is the triple bottom line assessment, implemented through a 'Life Cycle Sustainability Assessment' (LCSA) sensu Klöpffer and Grahl [25]. It consists of a Life-Cycle-Costing (LCC), an environmental Life-Cycle-Assessment (LCA), and a Social-Life-Cycle-Assessment (SLCA) of the biomass conversion systems to be assessed (see Fig. 2.1). The first step within the LCSA is to select appropriate assessment criteria from all triple line categories and then gathering or producing appropriate data for the decision making step.

2.2.2.1 Criteria selection

The most commonly applied evaluation criteria for renewable energy assessments are 'energy efficiency', 'technological maturity', 'investment' and 'production costs', 'greenhouse gas (GHG) emissions', 'land use', 'social acceptance' and 'job creation' [26]. Corresponding

assessment criteria specifically for biomass conversion systems can also be extracted from the literature (summarized in Tab. 2.1).

From the economic perspective, criteria typically used are ‘Production costs’, ‘Specific investment’ and the ‘Entrepreneurial risk of investment’. While almost all economic criteria (Tab. 2.1) are easy to quantify, the ‘Entrepreneurial risk of investment’ requires a clear definition about the meaning of a ‘risk’. A risk assessment then is dependent on subjective evaluation, and can therefore only be evaluated on a qualitative scale. The use of ‘Net present value’, ‘Return on investment,’ and ‘Return on equity’ moreover requires a substantial knowledge of the market in terms of sales volume and prices of the desired products. It therefore is based on a large number of market assumptions. Conversely, ‘Production cost’ and ‘Specific investment’ assessments can be carried out based on a pure costing approach. Corresponding data can easily be derived from the TDA carried out, and is less dependent on market assumptions. Although these criteria neglect the market perspective, the authors prefer their use.

‘Global warming potential (GWP)’, ‘Natural land use’ (which includes land consumption, soil degradation and their corresponding duration), and ‘(Fossil) Resource depletion’ are the most common criteria from the environmental perspective. GWP directly addresses climate change, whereas the other two criteria are linked to the ‘*trilemma challenge of bioenergy’* [5]. They are therefore as important as GWP in the assessment of bioenergy systems. The application of other criteria should be more or less dependent on the regional scope of the assessment carried out. Especially ‘Water consumption’ is expected to play a more crucial role for bioenergy assessment in the future. However, it is emphasized by Efroymson et al. [40] that environmental criteria should always be selected with regard to the use context.

From the societal point of view, questions pertaining to ‘Jobs created’, the ‘Competition for fertile land’ and the ‘Increased rural development’ remain the most frequently applied criteria

(see Tab. 2.1). Complementary criteria can also be any kind of 'social preferences' for specific biomass and energy sources [41–44] or the 'willingness to pay' for specific biomass technologies [45, 46]. In the end selection of the societal criteria is dependent on the number and different kind of stakeholders involved within the specific decision making situation.

Tab. 2.1: Typical MCDM criteria for bioenergy systems and biomass conversion processes form various sources (most commonly used criteria highlighted in bold).

Category	Criteria found (or similar)	References	Total Number
Economy	Net Present Value (NPV)	[24, 27]	2
	Production Costs	[16, 17, 19, 22, 24, 27–31]	**10**
	Specific Investment	[16, 17, 20, 24, 27, 29, 31]	**7**
	Gross Margin	[16, 27, 29, 31, 32]	5
	Return on Investment (ROI)	[29, 31, 33]	3
	Return on Equity (ROE)	[31]	1
	Entrepreneural Risk of Investment	[17–20, 28, 30, 33, 34]	**7**
Environment	Global Warming Potential (GWP)	[16, 17, 19–22, 24, 28, 29, 31, 32, 34–39]	**17**
	Acidification Potential	[18–20, 24, 32, 37, 38]	7
	Eutrophication Potential	[18, 24, 28, 31, 33]	5
	(Fossil) Resource Depletion	[18, 20, 24, 29, 33, 35, 37–39]	**9**
	Water Consumption	[22, 24, 31, 35, 37]	5
	Natural Land Use (Change and Duration)	[17, 18, 22, 24, 28, 31, 32, 34, 35, 37, 38]	**11**
	Ozone Depletion	[24, 38]	2
	Fine Dust Emissions	[24, 30, 33]	3
	Photosmog	[24, 38]	2
	Human Intoxication	[18, 24, 31, 38]	4
	Eco Toxicity	[24]	1
	Ionising Radiation	[24]	1
Society	Competition for Fertile Land	[18, 21, 22, 28, 30, 31, 34, 37, 38]	**9**
	Jobs Created	[16–18, 21, 22, 29–31, 33, 34, 37, 39]	**12**
	Increased Rural Development	[16–18, 20–22, 28, 31, 34, 36, 37, 39]	**12**
	Energy Supply Security	[16, 18, 20, 21, 30, 37]	6
	Public Acceptance Potential	[17–21, 31, 33, 37]	8
	Total Investment Inducement	[16, 39]	2

For the above-mentioned reasons, Tab. 2.1 should generally be regarded as a criteria portfolio. Based on the specific decision problem to be addressed, the most relevant criteria should be selected and applied. Nevertheless Tab. 2.1 does not claim to be complete and should be complemented where appropriate. Especially most of the economic criteria named refer to the traditional neoclassic perspective which completely leaves out external effects from the use of biomass. To better account for the total economic value, it also might be appropriate to

include such quantified external effects into the assessment as they are for instance have been reviewed by Solino et al. [47].

However, it cannot be assumed that the use of more and more criteria leads to better evaluation results [26]. Criteria selection should be undergone carefully, according to established methodologies and principles [48, 49].

2.2.2.2 Data gathering and production

The most obvious way to gather research data is through an extensive review of existing literature. A comprehensive review might yield all data needed, especially with regards to matured or popular biomass conversion processes and systems. However, a necessary precondition is that the collected data needs to be highly compatible to the process flow sheets established during the TDA and that it conforms to the same determined system boundaries and functional units. As reference flows and units these should be valid for the whole assessment. For premature or emerging processing technologies, it is likely that conclusive data sets cannot be drawn from literature. In this case it is necessary to obtain original data by applying established methodologies from the LCSA assessment tool box and conducting experimental research. It is imperative that the data produced matches the same system boundaries and functional unit(s) [25] as determined throughout the TDA.

Data production for economic criteria

Data quality and reliability is most important for reproducibility. Therefore, it is necessary to apply matured and established methods for data production. For the production of economic data, the *Life-Cycle-Costing* (LCC) approach is highly recommended. LCC has been successfully applied in a number of bioenergy assessments [50–53] and is broadly employed in industrial and administrational decision making. The basic principles of LCC have diligently been described by VDI-guideline 2884 [54] and elsewhere in literature [55–57].

While executing detailed LCC this method needs to be complemented by established cost estimation approaches summarized by example in [58] and [59]. Beside mathematical cost calculation approaches, simple cost statistics can also be adopted for that purpose.

Data production for environmental criteria

Environmental data production has already diligently been defined in the international standard ISO 14040 as *Life-Cycle-Assessment* (LCA) [60]. Moreover, detailed instructions and recommendations for LCA are readily available in the literature [25, 61–63]. However, a number of reviews critically point out that a real standard, defining framework conditions for the execution of LCAs in the context of biomass and bioenergy systems, has not been set so far [64], [65]. Such a standard should at least include recommendations about (i) the system boundaries, (ii) the allocation methods of impacts to main and side products, (iii) the impact categories (or assessment criteria) and (iv) the functional unit to be determined [66]. With its guideline VDI 6310 on *'Classification and quality criteria of biorefineries'* the German VDI proposed a first concept to partially standardize evaluation criteria for biorefineries [24]. Our UAF incorporates most of the VDI recommendations for LCSA. Additionally, to better account for dynamic indirect and locality-specific effects, an increasing number of studies are recognizing the value of consequential LCA in a bioenergy context as well [67, 68].

Data production for societal criteria

Although the United Nations Environment Programme (UNEP) and the Society of Environmental Toxicology and Chemistry (SETAC) have published '*Guidelines for social life-cycle assessment*' a number of years ago [69], an international standard for the execution of Social Life-Cycle Assessments (SLCA), equal to the ISO 14044 for LCA, is currently lacking. However, there is consensus in the literature, that SLCA needs to be executed in LCSA for the improvement of the framework conditions of different stakeholders within a production system. SLCA is in this case also regarded as a tool for the support of decision

making [70]. System boundaries in which SLCA takes place should be on a par with the system boundaries defined for the technical process (TDA). This does not necessarily imply that these system boundaries should be singularly derived from LCA, LCC, or SLCA. Moreover, the analysis of the needs of all three aspects should lead to a common system boundary definition, applied within the TDA and commonly used for LCSA [71, 72].

Concerning the guidelines previously mentioned [69], the stakeholders affected by products and production systems are first-line workers, local communities, the society, consumers and other value chain actors (e.g. such as civil service employees and politicians). Jørgensen et al. [72] therefore recommend narrowing SLCA in practice to the most relevant stakeholders within the system boundaries defined. These stakeholders can then merely be workers, local communities and the society, leaving out the rest of the above-mentioned for bioenergy.

Further, corresponding assessment criteria need to be deduced, applying functional units where possible. Tab. 2.2 (derived from [69]) attempts to assign different criteria to stakeholders and proposes appropriate scale types for the functional units where applicable. Recent work [73] shows that quantitative approaches for the assessment of the criteria 'Jobs created' and 'Rural development' are under development. Moreover, valuation studies with regard to stakeholder preferences for certain technologies and their 'willingness to pay' for can easily be used to complement the societal dimension of LCSA [41–46].

Tab. 2.2: Assignment of different social criteria to stakeholders involved and proposal of inventory indicators per functional units.

Stakeholders	Criterion	Criterion type	Inventory indicator (per functional unit)
Workers	Jobs created	quantitative	Induced working hours
Local community	Rural development	qualitative	-
Society	Competition for fertile land	qualitative	-
	Energy supply security	qualitative	-
	Public acceptance	qualitative	-
	Investment inducement	quantitative	Induced investment

2.2.3 Multi-Criteria Based Benchmarking – the decision making level

This paper has already described some of the general steps to be followed for the execution of a MCDM approach [74]. A detailed survey of different MCDM approaches and also their application for bioenergy systems has already been provided by Buchholz et al. [30]. The decision making step of the UAF proposed here is also a MCDM approach (decision making level). It was tailored specifically to the needs of the proposed architecture and is called *Multi-Criteria Based Benchmarking* (MCBB). In general it is possible to use other MCDM approaches, but in this case it has to be considered carefully, whether these approaches completely address the triple bottom line of sustainability, give strict definitions for the process design assessment and good foundation for unpretentious visualisation of the results. Subsequently, the algorithm is described mathematically.

2.2.3.1 Weighting categories and factors

The algorithm starts with the selection of the *weighting factors* $f_{w,s}$ for the different LCSA categories and the calculation of the so called *normalized category weighting factors* $f^N_{w,s}$ (with $s \in \{1 = \text{Economy}, 2 = \text{Environment}, 3 = \text{Societal}\}$):

Eq. 2.1: $$f_{w,s} \in \mathbb{R}^+$$

Eq. 2.2: $$f^N_{w,s} = \frac{f_{w,s}}{\sum f_{w,s}} \text{ with } \sum f^N_{w,s} = 1$$

Weighting is applied according to the importance of the single LCSA categories and their criteria. This weighting directly influences the result and therefore the output of the MCDM ranking. In case of MCBB it is recommended, to begin with the weighting of the different LCSA categories (depicted in Fig. 2.1) which constitute the triple bottom line [25].

From the definition of sustainability it can be derived that within the triple bottom line a trade-off between the different categories needs to be achieved. From a scientific point of view there does not seem to be a rational reason to under- or overweight one of these LCSA categories [75], as sustainability is always demanding to balance these three aspects [76, 77].

For the execution of this methodology we therefore recommend the application of the *equal weights method* [78, 79] for category weighting. However, weighting is an overall important step within MCDM approaches which apart from scientific considerations can also be quite subjective. Often there exists a complex hierarchy of categories, criteria, and sub-criteria. Besides applying the equal weights method it can be necessary to assess these hierarchies in more detail and to apply a deviant weighting, based on expert judgments and literature reviews. In this regard van Til et al. [80] recently examined the impact of different weighting techniques on criteria weighting. They found that within group decisions, the use of different elicitation techniques has minor influence on criteria weights. In contrast, when weighting is applied for individual decision support, the application of different elicitation methods leads to deviant weighting results which then yield study results that hardly can be compared.

However, these considerations are quite complex and therefore far beyond the scope of this paper. It is important, that weighting needs to be considered diligently by the user of this methodology. For the demonstration of the MCBB approach with random test data in Section 2.5 we simply apply the equal weights method for category weighting. Using the mathematical approach, in combination with Eq. 2.1 and 2.2, this leads to:

Eq. 2.3: $f_{w,s}^{N} = \frac{1}{s}$ with s = 3

The result of Eq. 2.3 is that, regardless of how many criteria are chosen inside one of the LCSA category s, the outside category dispartment always remains equal to the others. If necessary, MCBB in general offers the possibility to weight the categories differently by freely applying Eq.2.1 and 2.2.

2.2.3.2 Criteria selection and criteria type determination

The next step includes the selection of the relevant assessment criteria $E_{i,s}$ (with $i \in \{1 \dots n_s\} \subseteq \mathbb{N}^+$ and $\sum n_s$= n) which will be involved in the biomass conversion system

assessment. Necessarily, these criteria need to be chosen and assigned to one of the LCSA categories s. Subsequently, the criteria type K_i needs to be determined.

Eq. 2.4: $$K_i = \begin{cases} 0 \\ 1 \end{cases}$$

As shown in Eq. 2.4 K_i can either be 0 or 1. For each $E_{i,s}$ the value will be set to 0 if $E_{i,s}$ is positively correlated with the assessment, which means that high criteria values show a good system performance. Otherwise K_i will be set to 1 if the value of $E_{i,s}$ is negatively correlated, which means that high criteria values show a bad system performance.

2.2.3.3 Selection of criteria weighting factors and calculation of weighting angles

The following step is the assignment of the *criteria weighting factors* $w_{i,s}$ to the different criteria $E_{i,s}$, the calculation of the corresponding *normalized weighting factors* $w^N_{i,s}$, and further the calculation of the *weighting angles* α_i needed for visualization:

Eq. 2.5: $$w_{i,s} \in \mathbb{R}^+$$

Eq. 2.6: $$w^N_{i,s} = \frac{w_{i,s}}{\sum_{i=1}^{n_s} w_{i,s}} \text{ with } \sum_{i=1}^{n_s} w^N_{i,s} = 1$$

Eq. 2.7: $$\alpha_i = f^N_{w,s}\, w^N_{i,s} \times 360°$$

If the equality principle will also be applied for criteria weighting, Eq. 2.6 would be reduced to:

Eq. 2.8: $$w^N_{i,s} = \frac{1}{n_s}$$

Nevertheless, in some cases it might be useful to over- or underweight certain criteria inside a category. This could be due to their relative importance to the assessment or due to redundancies between single criteria (see also Section 2.2.3.1). While this condition applies, different *rank-order weighting methodologies* can be deployed to determine the correct

measures. Rank-order methods have extensively been reviewed by [26] and can also be studied in [81]. For the demonstration of the MCBB approach with random test data in Section 2.3 we applied random weighting factors apart from the equality principle for the criteria inside the categories.

2.2.3.4 System selection and data research

Selection of the biomass conversion system and data acquisition is the most elaborate task of this methodology. At first, the kind and number m of different biomass conversion systems which should be assessed need to be selected (with $j \in \{2 \dots m\} \subseteq \mathbb{N}^{+}$). Then extensive data research has to be conducted to gather appropriate values X_{ij} for every single process m and criteria $E_{i,s}$. Within this step, gaps in the availability of scientific data will be revealed. To bring MCBB to a successful MCDM assessment it might be necessary to set up experiments and measurements to produce the relevant data needed in order to progress with the above described LCSA methods (see Section 2.2.2.2). The overall aim of this step is to compose and complement the so called *criteria value matrix C*. Its completion is essential to proceed with this methodology.

Eq. 2.9: $$C = \begin{pmatrix} X_{11} & \cdots & X_{n1} \\ \vdots & \ddots & \vdots \\ X_{1m} & \cdots & X_{nm} \end{pmatrix}$$

2.2.3.5 Normalizing and weighting the criteria value matrix

For the normalization of C the use of an adjusted *zero-one normalisation method* [82] is recommended. Therefore, in the beginning it is necessary to extract the maximum and minimum value vectors V^{max} and V^{min} from C. These values are needed to calculate the *normalized criteria values* X^{N}_{ij} within the *normalized criteria value matrix* C^{N}:

Eq. 2.10: $$V^{max} = \begin{pmatrix} X_{1j}^{max} & \cdots & X_{nj}^{max} \end{pmatrix}$$

Eq. 2.11: $$V^{min} = \begin{pmatrix} X_{1j}^{min} & \cdots & X_{nj}^{min} \end{pmatrix}$$

C^{N} is then calculated as follows:

Eq. 2.12: $$C^N = \begin{pmatrix} X_{11}^N & \cdots & X_{n1}^N \\ \vdots & \ddots & \vdots \\ X_{1m}^N & \cdots & X_{nm}^N \end{pmatrix} \text{with}$$

Eq. 2.13: $$X_{ij}^N = \begin{cases} \frac{X_{ij} - X_{ij}^{min}}{X_{ij}^{max} - X_{ij}^{min}} & K_i = 0 \\ 1 - \frac{X_{ij} - X_{ij}^{min}}{X_{ij}^{max} - X_{ij}^{min}} & K_i = 1 \end{cases}$$

The zero-one normalisation method simplifies data standardisation as it implies a linear relationship; however that might be not the case in reality. In statistic literature a large number of different data standardisation approaches exist. In this regard Milligan and Cooper [83] give a brief overview of relevant approaches involving numerical variables. The user of this methodology is therefore strongly encouraged to find out about e.g. cluster in the data applied and to use deviant normalisation approaches as appropriate.

To consider the weighting made by Eq. 2.2 and 2.6 appropriately the *normalized and weighted criteria value matrix A* needs to be calculated from C^N:

Eq. 2.14: $$A = \begin{pmatrix} A_{11} & \cdots & A_{n1} \\ \vdots & \ddots & \vdots \\ A_{1m} & \cdots & A_{nm} \end{pmatrix} \text{ with}$$

Eq. 2.15**:** $$A_{ij} = f_{w,s}^N \times w_{i,s}^N \times X_{ij}^N$$

2.2.3.6 Calculation of the benchmarking vectors

The final step of the algorithm is the calculation of the results itself in the form of the unweighted (B^u) and weighted (B^w) *benchmarking vector*s:

Eq. 2.16: $$B^u = \begin{pmatrix} b_1^u \\ \vdots \\ b_m^u \end{pmatrix} \text{ with}$$

Eq. 2.17: $$b_j^u = \frac{\sum_{i=1}^n X_{ij}^N}{n} \times 100\ \%$$

Eq. 2.18: $$B^w = \begin{pmatrix} b_1^w \\ \vdots \\ b_m^w \end{pmatrix} \text{with}$$

Eq. 2.19: $b_j^w = \sum_{i=1}^{n} A_{ij}$

2.2.3.7 Visualization of the benchmarking results

The visualization of the benchmarking results is an additional but essential step within MCBB. MCDM approaches are often criticized because of the aggregation of data in combination with criteria weighting, which is assumed to be quite non-transparent.

For the visualization of the weighted benchmarking results MCBB uses *advanced radar plots* (ARP), which have been adapted for the demands of this methodology [84]. They are making the single criteria values A_{ij} transparent for system j and their specific weighting. The circle sectors in ARPs directly show the fractional values of A_{ij} for each process technology j corresponding to every assessed criterion. For each biomass conversion system j, a single ARP can be drawn and compared with others.

ARPs are based on a circle illustration with n axes, starting in the center of the circle, one axis for every criterion involved in the assessment. The nominal radius of the ARP circle is by definition set to $(1/\pi)^{1/2}$ derived from the standard circular area equation. The circle area is therefore by definition always equal π square units and can be multiplied with f_v as scaling factor for a better sizing and readability of the chart. The value of f_v should be appropriately selected from $\mathbb{R}^+$, whose unit generally is centimeters or millimeters. The radius for the standard circle *r* is calculated as follows:

Eq. 2.20: $r = \left(\frac{1}{\Pi}\right)^{\frac{1}{2}} \times f_v$

For the labeling of the values within the chart it is recommend to use the origin values A_{ij} to ensure better comparability with B^W, indicating in the chart description that they have been multiplied with f_v. As the circle sector areas should be equal to the single values of A, the

ARP radius matrix r needs to be calculated. Its values are the base for the following drawing instructions. The values of R also need to be multiplied by f_v.

Eq. 2.21: $$R = \begin{pmatrix} r_{11} & \cdots & r_{n1} \\ \vdots & \ddots & \vdots \\ r_{1m} & \cdots & r_{nm} \end{pmatrix} \text{ with}$$

Eq. 2.22: $$r_{ij} = \left(\frac{X_{ij}^N}{\Pi}\right)^{\frac{1}{2}}$$

Fig. 2.3 gives an example for an advanced radar plot with detailed illustration of the single values. The ARP has to be segmented into the corresponding LCSA weighting categories s by the corresponding category angles (see Eq. 2.23).

Eq. 2.23: $$\alpha_s = f_{w,s}^N \times 360°$$

The Eq. 2.3 implies that $f_{w,s}^N$ is equal to 3 and thus α_s is equal to 120°.

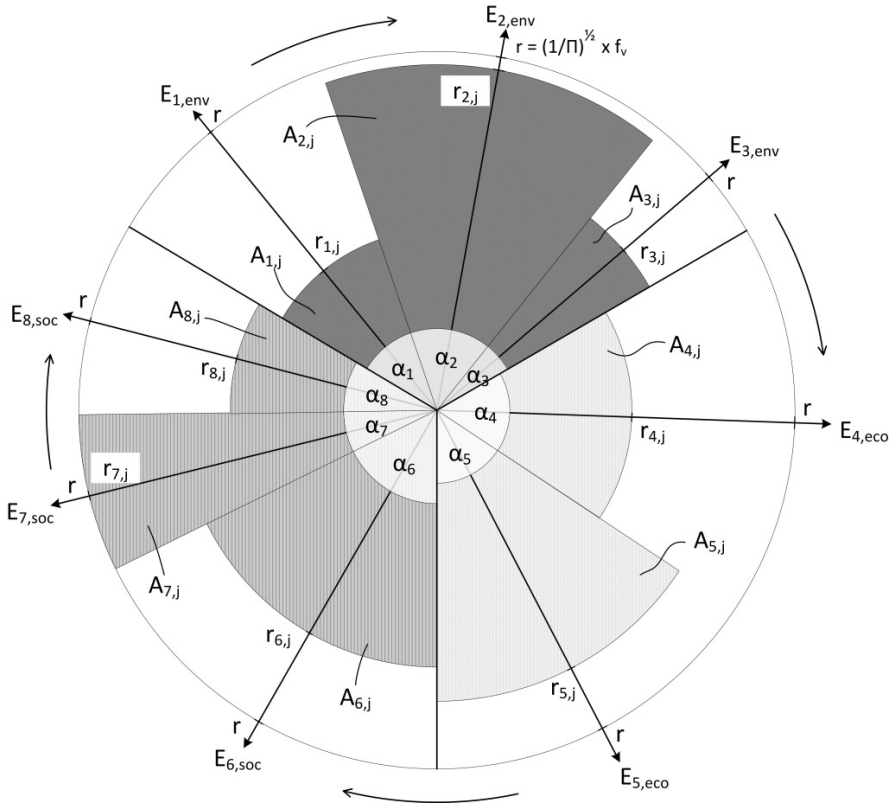

Fig. 2.3: Example for an advanced radar plot drawing for biomass conversion system j.

An overview of the abbreviations and variables used within MCBB is given in Tab. 2.3.

Tab. 2.3: Variables used in the MCBB approach.

Variables	Definition
A	Normalized and weighted criteria value matrix.
A_{ij}	Normalized and weighted criteria value for criteria I and biomass conversion system j.
B^u	Unweighted benchmarking vector.
b^u_j	Unweighted benchmarking value for biomass conversion system j.
B^w	Weighted benchmarking vector.
b^w_j	Weighted benchmarking value for biomass conversion system j.
C	Criteria value matrix.
C^N	Normalised criteria value matrix.
$E_{i,s}$	Assessment criteria no. i part of category s.
$f^N_{w,s}$	Normalised weighting factor for the category s.
f_v	Scaling factor for ARPs.
$f_{w,s}$	Weighting factor for the category s.
i	Sequential no. of criteria.
j	Sequential no. of biomass conversion system.
K_i	Type of criteria i.
m	Total no. of biomass conversion systems.
n	Total no. of criteria.
n_s	Total no. of criteria within category s.
r	Radius of the ARP standard circle.
R	ARP radius matrix.
r_{ij}	Radius value for criteria i and biomass conversion system j.
V^{max}	Maximum value vector.
V^{min}	Minimum value vector.
$w_{i,s}$	Weighting factor for criteria i within category s.
$w^N_{i,s}$	Normalized weighting factor for criteria i within category s.
X_{ij}	Criteria value for criteria i and biomass conversion system j.
X^N_{ij}	Normalized criteria value for criteria i and biomass conversion system j.
α_i	Weighting angle of criteria i.

2.2.3.8 Selection procedure

Based on the benchmarking vectors and the ARPs the selection procedure can be started. As all aspects relevant to decision making have already been covered previously by the weighting procedure of categories and criteria, the selection of the option with the highest overall benchmark or assessment score is appropriate. However, it might be useful from the stakeholders' perspective to discuss the results of the best three to five alternatives again with respect to their constitution on the basis of the ARPs and to criteria weighting. It might also be necessary to rethink criteria weighting again and to adjust it iteratively.

2.3 Calculation

In the following the functionality of the decision making level of the proposed architecture is demonstrated by random test data.

The data provided in Tab. 2.4 is descriptive meta-data for a random test set of numbers (Tab. 2.5). These data is given for the assessment of three different biomass conversion systems in three weighting categories s: societal (SOC), environment (ENV) and economy (ECO). From Tab. 2.4 follows that, for category number 2 there will be three weighting criteria included in the decision making process, namely *'Natural land use'*, *'GWP'* and *'Fossil resource depletion'*. In each of the other two weighting categories only two criteria will be applied. For category 1 these are the criteria *'Jobs created'* and *'Increased rural development'* and for category 3 *'Production costs'* and *'Specific investment'*. The corresponding units (in the case of MCBB called dimension D_i) are also given.

Tab. 2.4: Descriptive meta-data for the random test data set in Tab. 2.5 for the demonstration of MCBB including criteria numbers i, weighting category classification, physical units, correlation type K_i, (normalized) weighting factors ($w_{i,s}^N$ *and* $w_{i,s}$) and angles α_i.

Criterion $E_{i,s}$	Jobs created	Increased rural development	Natural land use	GWP	Fossil resource depletion	Production costs	Specific investment
Criterion number	1	2	3	4	5	6	7
Weighting category s	SOC	SOC	ENV	ENV	ENV	ECO	ECO
Dimension D_i	(3,600 s)/GJ	-	MJ/(10^4 m²)	(10^{-3} kg_{CO2eq})/MJ	MJ/MJ_{pri}	€/MJ	€/MW
Correlation type K_i	0	0	1	1	1	1	1
Weighting factor $w_{i,s}$	8	2	2	7	1	3	1
Normalized weighting factor $w^N_{i,s}$	0.80	0.20	0.20	0.70	0.10	0.75	0.25
Criteria weighting angle α_i (°)	96.00	24.00	24.00	84.00	12.00	90.00	30.00

SI-unit explanation: 3,600 s = 1 hour; 10^4 m² = 1 hectare; 10^{-3} kg = 1 gram.

Except for criterion number 2 it is assumed that all criteria can be measured quantitatively. Criterion number 2 will solely be measured qualitatively by a scale from 1 (no rural development induced) to 9 (extraordinary rural development induced). Only criteria number 1 and 2 are positively correlated to the process assessment. This means that high values show good and low values bad performance with regard to the system assessment. For these criteria the value of K_i is therefore set to 0. The remaining criteria are negatively correlated; therefore K_i has been set to 1.

Tab. 2.5: Random test data and calculations for the demonstration of the MCBB approach.

Biomass conversion system No.	Criterion No.						
	1	**2**	**3**	**4**	**5**	**6**	**7**
C : Criteria value matrix (random test data)							
1	0.045	8	90.0	25.0	20.0	0.03	4.000
2	0.06	4	100.0	10.0	18.0	0.04	2.500
3	0.02	5	75.0	45.0	30.0	0.025	1.200
C^N : Normalized criteria value matrix (random test data)							
1	0.6250	1.0000	0.4000	0.5714	0.8333	0.6667	0.0000
2	1.0000	0.0000	0.0000	1.0000	1.0000	0.0000	0.5357
3	0.0000	0.2500	1.0000	0.0000	0.0000	1.0000	1.0000
A : Weighted and normalized criteria value matrix							
1	0.1667	0.0667	0.0267	0.1333	0.0278	0.1667	0.0000
2	0.2667	0.0000	0.0000	0.2333	0.0333	0.0000	0.0446
3	0.0000	0.0167	0.0667	0.0000	0.0000	0.2500	0.0833
R : Advanced radar plot matrix							
1	0.4460	0.5642	0.3568	0.4265	0.5150	0.4607	0.0000
2	0.5642	0.0000	0.0000	0.5642	0.5642	0.0000	0.4129
3	0.0000	0.2821	0.5642	0.0000	0.0000	0.5642	0.5642

Eq. 2.3 is applied for the external weighting of the categories. This means that within the example the triple bottom line of sustainability is weighted equally, although inside the categories a different number of criteria are applied. The internal category weighting factors $w_{i,s}$ are shown in Tab. 2.4. The direct results from the application of Eq. 2.6 and 2.7, the calculated normalized weighting factors $w^N_{i,s}$ and the criteria weighting angles α_i are illustrated as well. Tab. 2.5 presents the criteria value matrix C as a result from data gathering and production. From C the two vectors V^{max} and V^{min} will be produced:

Eq. 2.24: $$V^{max} = (0.06; 8; 100; 45; 30; 0.04; 4000)$$

Eq. 2.25: $$V^{min} = (0.02; 4; 75; 10; 18; 0.025; 1200)$$

Subsequent to the use of Eq. 2.10, 2.11 and 2.13, the normalized criteria value matrix C^N can be calculated (also shown in Tab. 2.5). Furthermore, the application of Eq. 2.14 and 2.15 lead to matrix A (see Tab. 2.5). C^N and A then result in the decision vectors B^u and B^w via Eq. 2 17 and 2.19:

Eq. 2.26: $$B^u = \begin{pmatrix} 58{,}5\% \\ 50{,}5\% \\ 46{,}4\% \end{pmatrix} \begin{matrix} Biomass\ conversion\ system\ 1 \\ Biomass\ conversion\ system\ 2 \\ Biomass\ conversion\ system\ 3 \end{matrix}$$

Eq. 2.27: $$B^w = \begin{pmatrix} 58.8\% \\ 57{,}8\% \\ 41{,}7\% \end{pmatrix} \begin{matrix} Biomass\ conversion\ system\ 1 \\ Biomass\ conversion\ system\ 2 \\ Biomass\ conversion\ system\ 3 \end{matrix}$$

Through comparison of these decision vectors it can be derived, that weighting of the criteria inside the weighting categories pushes biomass conversion system 2 closer to the result of biomass conversion system 1 which represents the best benchmarked system and should therefore be selected. Finally, within the example the weighting process causes a setback of biomass conversion system 3 (see Tab. 2.5).

For the production of the ARPs matrix R needs to be calculated (see Tab. 2.5). Following the instructions above the combination of the weighting angles α_i and matrix R leads to the ARPs depicted in Fig. 2.4. In which scaling factor f_v is defined as:

Eq. 2.28: $$f_v = \left(\frac{1}{\Pi}\right)^{-\frac{1}{2}} \times z\ 10^{-3}\ m$$

Based on Eq. 2 28 the ARPs can then be drawn in a reasonable size.

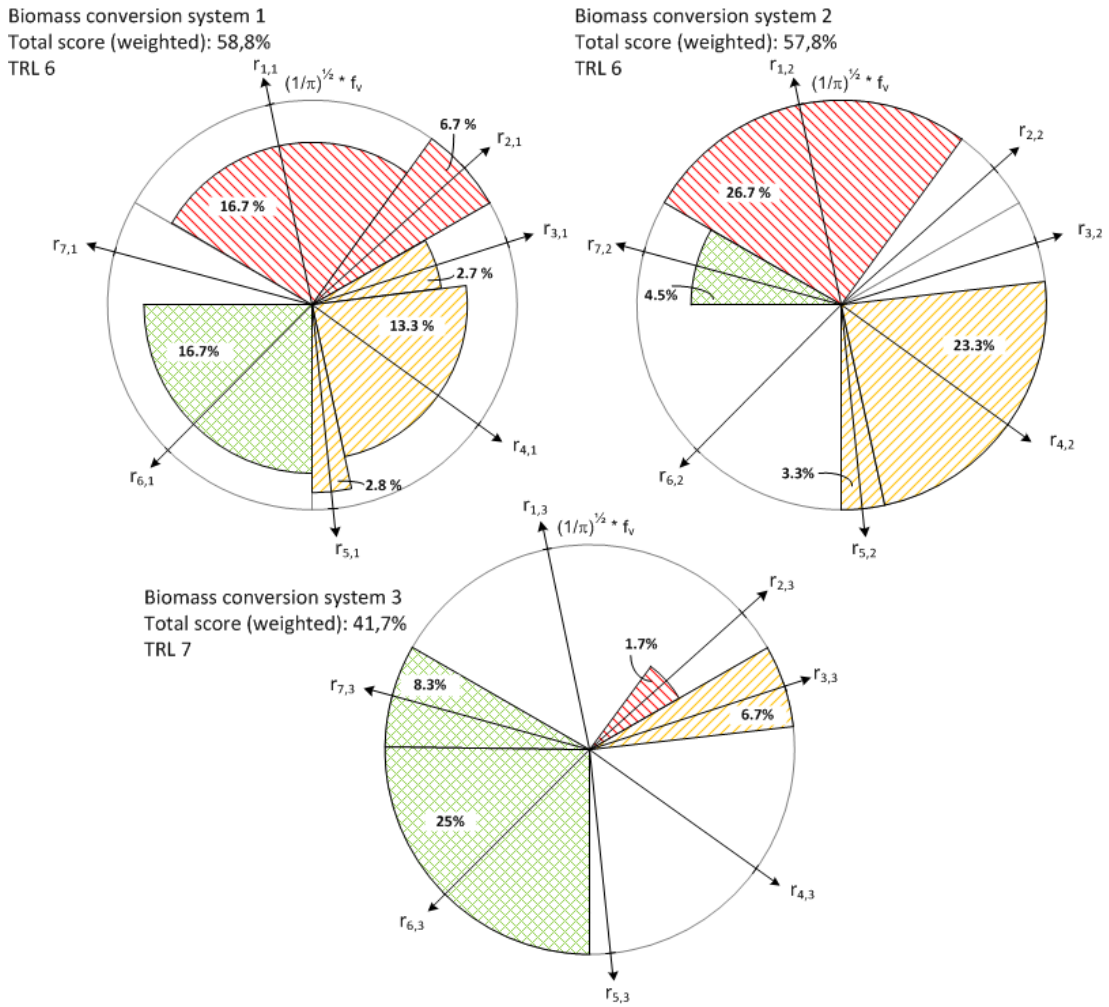

Fig. 2.4: Advanced radar plots (ARP) as MCBB result from the basic test data example.

2.4 Results and discussion

Although biofuels assessments and other more integrated approaches for an UAF have already been published, this is the first time that an integrated approach for biomass conversion systems is presented that addresses major requirements from literature in a more generalized form. Further, it compiles all necessary aspects in complete appraisal architecture and therefore goes beyond all existing appraisal frameworks. On the data, impact and decision making level its structured modus operandi lays the foundation to generate substantial and comparable data about the extent, meaning and diversity of impacts and the key problems of biomass domains which currently still are afflicted with uncertainties [1]. The application of this UAF approach can lead to the improvement of existing and future policies and can give

bioenergy a better foundation within the ethical debate by transparently showing the trade-offs between economy, environment and society.

In this respect also results from environmental economics are of high relevance. These can easily be incorporated into the assessment and offer the opportunity to deliver appraisal results that go for instance beyond neoclassical economics by considering external effect from cultivation, conversion and use of biomass. Additionally valuation studies, which measure the 'willingness to pay' of stakeholders for a certain technology, can complement the weak structured SLCA assessment and can therefore be utilized to complete the societal appraisal pillar of the architecture.

Beside these advantages it also has to be stressed that the UAF proposed might risk limiting the range of choices to those for which detailed data is available. However, this objection would apply to all thinkable appraisal frameworks. It is therefore necessary to mention that the proposed approach not also keeps recommendations about the possible assessment order but also about data production. Stakeholders using it for decision making should be aware that data production for especially new biomass conversion systems might take its time. Quick decisions are not always possible in this context.

To even stronger emphasize uncertainties related to the technology systems assessed, the decision making level can be extended and improved by e.g. the concept of *Technology Readiness Levels* (TRL) [85–87]. Taken as an inverse uncertainty level, TRL is able to give an indication about the maturity of a certain biomass conversion system or technology and therefore an indication about general data reliability. For a proper application of this UAF there still is some research to be done with regard to a transparent selection of appropriate decision criteria, the development and qualitative measurement of especially criteria from SLCA, and of course with regard to criteria and category weighting. Weighting is always of major relevance for a proper application and is the interface between analyst and stakeholders.

2.5 Conclusions

An integrated approach for a UAF for biomass conversion systems has been presented and its application was demonstrated by random test data on the decision making level. It includes thoroughly executed technology analysis by Technology Design Assessments on the data level, addressing the need of impartiality, scientific evidence basis, and comparability of different assessment results by standardisation. Explicit values and ethics are incorporated by the use of the triple bottom line approach of sustainability on the impact level. The embedment of well documented, matured tools and methodologies also addresses the need for transparency and gives the possibility to better examine the interdependencies of environmental, economic and social criteria [4]. On the decision making level a tailor-made multi-criteria decision making method (MCBB) is proposed which can be applied for an undetermined number of different biomass conversion systems. Further, ARPs are used for transparent and easy visual comparison of different policy options. These two features do not only address the need for impartiality and transparency, they also include the necessary interfaces for the participation of lay people, experts, and stakeholders during the weighting and decision making procedure [3]. Environmental economics and societal valuation studies can complement the economic and societal dimension of the approach proposed. This UAF goes beyond the literature on bioenergy appraisal frameworks and can be used as a baseline for future work.

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SECTION 3

PREDICTION OF GASEOUS, LIQUID AND SOLID MASS YIELDS FROM HYDROTHERMAL CARBONIZATION OF BIOGAS DIGESTATE BY SEVERITY PARAMETER[3]

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3. PREDICTION OF GASEOUS, LIQUID AND SOLID MASS YIELDS FROM HYDROTHERMAL CARBONIZATION OF BIOGAS DIGESTATE BY SEVERITY PARAMETER

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Abstract

The product yields of hydrothermal carbonization of digestate as well as the degree of carbonization of hydrochar are quantified as functions of process parameters by using a severity approach. In contrast to other studies, a logarithmic dependence on process severity was applied. Process severity itself was calculated from temperature, retention time and catalyst concentration. Data gained from batch experiments (190–245 °C, 140–560 min) was used to fit the model parameters. By these models basing on few selected reaction conditions, a wide range of process conditions can be covered and the yields for the solid, liquid and gaseous product phase can be predicted. Moreover, the paper delivers model equations for the prediction of the H/C and O/C ratios for the solid product phase. Such model equations can be used for process optimization and are the foundation for proper LCA calculations. For the first time, the quantitative impact of the difference in reaction conditions on the product phase yield is described and analysed.

Keywords

hydrothermal carbonization, biogas digestate, severity parameter, model equations, mass balance, degree of carbonization

3.1 Introduction

Interest in hydrothermal carbonization (HTC) has increased since Titirici et al. [1, 2] published their key reviews in 2007. Since then, a large amount of papers were made public on this topic. While a few of these focus on the comparison of HTC with other processes, e.g. torrefaction [3], vapothermal carbonization [4] and pyrolysis [5–8], most others focus on a mixture of the usability of a certain biomass, process optimization, different utilization pathways for the hydrochar and the effect of different reaction parameters.

The kind of biomass examined ranges from model substances (e.g. pure cellulose, starch, lignin and glucose), over sewage sludge, agricultural residues, residual lignocellulosic biomass, wood and algae. On the other hand, the application of hydrochar ranges from soil amendment to gasification and combustion or as activated carbon, aerogels, nanoparticles and composite materials for, for example, electrical applications. For the influence of reaction parameters (e.g. process temperature, retention time, acid concentration, particle size of the biomass, dry mass to water ratio in the feedstock), mostly the qualitative effects of parameter variation on the properties of the HTC products have been described. The main findings on parameter variation are summarized below.

Danso-Boateng et al. [9] examined the effect of temperature and retention time during HTC of sewage sludge and described the resulting properties (elemental and material composition) of products (hydrochar and liquid and gas phase). Guiotoku et al. [10] characterized the hydrochar from cellulose-based renewable raw materials achieved at 200 °C (with 60-, 120- and 240-min reaction time) by proximate analysis, gross calorific value and thermo-gravimetric analysis. Reza et al. [11] examined the effects of process temperature and retention time on the solid product phase and process liquids from HTC of cellulose, poplar and straw. They found that the chemical content in the liquid product phase varied and that total sugars and furfural derivatives yield followed first-order degradation kinetics. Moreover,

the authors concluded that organic acid yield forms a maximum at HTC 230–250 °C and that phenolic substance were stable in the temperature range of 200–260 °C.

Yan et al. [12], Reza et al. [13] and Lynam et al. [14] carried out HTC experiments to explore the effects of reaction parameters on the resulting hydrochar produced from loblolly pine. Whereas Yan et al. applied temperatures between 200 and 230 °C, feedstock particle size 0.60–2.38 mm, and reaction times between 1 and 5 min, Reza et al. used temperatures of 200, 230 and 260 °C and retention times between 15 s and 30 min. Reaction temperature was found to have a much stronger influence on mass yield and higher heating value (HHV) than particle size or reaction time by [12]. Reza et al. [13] found that the solid product mass yield decreases rapidly within the first minutes of reaction and a first-order kinetic model was set up and validated for the mass yield of hydrochar. Lynam et al. used loblolly pine with a particle size of 1.168–0.589 mm at 260 °C for 5 min, and the impact of different ionic salts on the process pressure was examined. It was found that calcium chloride and calcium lactate addition increases HHV and decreases the process pressure.

Reza and Lynam et al. [15] carried out a series of experiments with corn stover, miscanthus, switch grass and rice hulls at 200, 230 and 260 °C for 5 min each. It was found that the mass yield was as low as 41 % of the raw biomass and decreases with increasing process temperature. The higher heating values increased up to 55%at the same time. Wiedner et al.[16] carried out experiments with poplar wood chips, solid olive residues and wheat straw at 180, 210 and 230 °C. They found that the chemical properties of the hydrochar varied with a change in temperature and to a much lesser extent also to feedstock. Roman et al. [17] studied HTC of walnut shell and sunflower stem under different conditions (190–230 °C, 20–45 h) and found that HTC brought up an increase on the heating value of 1.75- and 1.50-fold when compared with the biomass. The authors also claimed that temperature and water/biomass ratio were more influential on the process than residence time.

Hoekman et al. [18] applied a mixed wood feedstock to HTC and studied the effects of the reaction conditions on product compositions and yields by varying process temperature between 215 and 295 °C and retention time in the range of 5 to 60 min. They observed that with increasing temperature and time, the amount of the gaseous and liquid product phase increased, while the amount of hydrochar decreased. Moreover, the energy density of the char increased with reaction severity. Mumme et al. [19] took biogas digestate from maize silage and also cellulose for their HTC experiments. A Box-Behnken experiment design was employed with process temperatures of 190, 230 and 270 °C, retention times of 2, 6 and 10 h and pH values of 3, 5 and 7. They found that temperature was the most influencing factor on carbonization, whereas the different hydrochars produced differed largely in their chemical and structural properties.

From the literature review above, it can be seen that a lot of valuable work has been done on HTC so far. However, there is currently no paper that tries to focus on the complete mathematical/statistical description of the mass balance (solid, liquid and gaseous products) of the HTC process and the quantification of changes in the different product phase yields and the degree of carbonization. Complete mass balances and their mathematical description are essential for technology assessment and evaluation, e.g. life cycle assessment (LCA), and to optimize the process technology. The present work therefore focuses on this mathematical/statistical description by carrying out HTC experiments with biogas digestate at varying process conditions on the one hand and severity modelling on the other. The aim is to mathematically describe the change in the solid, liquid and gaseous process output by the variation of the process parameters.

3.2 Materials and Methods

Below, materials, equipment, and analytic methods are described. All experiments are carried out with digestate.

3.2.1 Materials

The biomass used was digestate from a mesophilic biogas plant operated in Filderstadt/Harthausen close to Stuttgart (Germany). The biogas plant was fed with a substrate mixture of 40 wt% corn silage, 30 wt% grass silage and 30 wt% liquid cattle manure. The dry mass (DM) content (ξ_{DG}) of the digestate was 6.73 wt% (number of samples taken: N=4; standard error: σ_N=0.05 wt%).

In order to produce homogeneous reactant slurry for the experiments, the digestate was first subject to a solid-liquid separation. For this purpose, the liquid was squeezed out by means of a silage press from HAPA at a pressing pressure of 5 MPa. The pressing water was collected, stirred, examined in four samples with respect to its DM content ($\xi_{DG,l}$=4.05 wt%; N=4; σ_N=0.05 wt%) and frozen in portions at −18 °C. The solid phase was spread evenly in an oven and dried at 40 °C to its weight balance. Further, the dried solid was crushed with a knife mill to a mesh size of 1 mm and smaller. The DM content of the solid was determined by three samples ($\xi_{DG,s}$=90.33 wt%; N=3; σ_N=1.06 wt%). Afterwards, it was stored under dry conditions in a closed container.

3.2.2 Experimental set-up

3.2.2.1 Citric Acid

To estimate the buffering capacity of the reactant slurry described below, the effects of adding citric acid were examined in a series of titration experiments with a 2 M citric acid solution. For this purpose, an automatic titrator from METTLER TOLEDO (type DL21) was used to perform 24-h continuous ‘pH Stat’ titration (LAGA standard EW 98) to set pH values to 3, 5 and 7. Each titration experiment was repeated once. Based on these tests, the required crystalline mass of citric acid, which was necessary for a corresponding significant and permanent change in the pH value of the reactant slurry, was calculated.

It was found that the slurry needed the following additions of crystalline citric acid to sustainably change the pH value: 0.078 g (pH 7), 0.144 g (pH 5) and 0.548 g (pH 3) citric acid

per g digestate dry mass. Carrying out the experiments later, the appropriate amount of citric acid was added in crystalline form.

3.2.2.2 Carbonization experiments

The carbonization experiments were conducted in a cylindrical 250-ml batch autoclave (h=110 mm, d=74 mm) made from stainless steel (1.4571). The autoclave was equipped with internal sensors for pressure and temperature connected to a data logger of Endress+Hauser (RSG30). The process temperature (T_p) applied was 190, 220 and 245 °C. Experiments were carried out for durations of 140, 320 and 560 min (d_R) where reaction time was measured from the point the reactors reached 180 °C. The initial additive (citric acid) concentrations (X) were 0.078, 0.144 and 0.548 g per g digestate (DM). A Box-Behnken experiment design was employed to reduce the number of runs to 15 including 3 centre points (CP) [19]. All of the 15 experiments have been repeated once. In total, 30 experiments have been carried out in random order. The different set-ups are illustrated in Tab 3.1 in more detail.

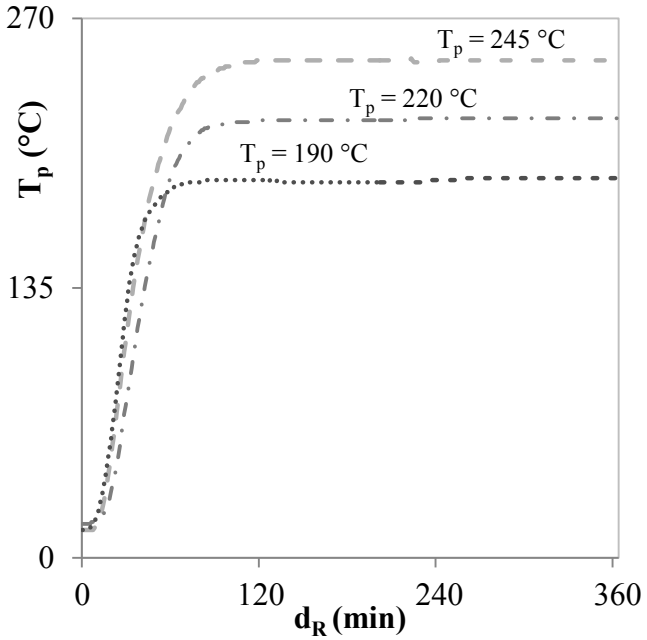

Fig. 3.1: Temperature profiles of the experimental set-up (duration 360 min).

Dried solids and defrosted press water were mixed to a total extent of 15 wt% DM of digestate directly in the batch. The mixture was homogenized by stirring and crystalline citric

acid was added. The reactor was weighted before and after filling. Through the gas valves, the autoclaves' free room was gas flushed with the inert gas argon.

Heating was performed in a repurposed gas chromatograph oven of Hewlett Packard (5890 Series II). Heating the batch reactor up to 180 °C took 40 min on average and then 35–45 min again to heat the content to the desired reaction temperature. The temperatures were maintained at the set-point for the desired reaction time. Different example temperature profiles, all with durations of 360 min, are illustrated in Fig. 3.1. According to Ruiz et al. [20] similar temperature profiles can be classified as isothermal for practical calculations, although they include the heating phase with increasing temperatures in the beginning.

At the end of the desired reaction time, the batch reactor was removed from the oven and cooled down to ambient temperature conditions by water quenching for 20 min. After this, the autoclave was diligently dried outside with a clean towel and connected to a gasometer. A gas sample was taken to analyse the gas composition.

Tab. 3.1: Experimental set-up and results from the HTC of biogas digestate: mass balances, elemental composition of the hydrochar, and energy content.

No.	T_p (°C)	X ($g_{CA}/g_{DG,DM}$)	d_R (min)	N	Y_s ($g_{s,DM}/g_{DM}$)		Y_ℓ ($g_\ell/g_{DG,DM}$)		Y_g (mg/g_{DM})		N	C (wt%)		H (wt%)		O (wt%)		H/C (-)		O/C (-)		HHV[a] (MJ/kg)	
					A	σ_N	A	σ_N	A	σ_N		A	σ_N	A	σ_N	A	σ_N	A	σ_N	A	σ_N	A	σ_N
1	190	0.078	320	1	0.5874		0.383		34.1		2	56.5%		7.1%		32.7%		1.49		0.43		24.84	
2	190	0.144	140	1	0.6358		0.413		41.9		2	56.4%		7.0%		33.0%		1.49		0.44		24.69	
3	190	0.144	560	2	0.6400		0.415		49.7		2	60.4%		7.1%		28.5%		1.40		0.35		26.61	
4	220	0.078	140	2	0.6187		0.372		62.6		2	61.2%		7.0%		27.8%		1.37		0.34		26.89	
5	220	0.078	560	2	0.5328		0.474		86.3		2	67.2%		7.3%		20.5%		1.29		0.23		30.14	
6	220	0.144	320	6	0.5673	0.01	0.464	0.02	74.7	1.7	6	62.6%	0.5%	7.0%	0.1%	26.0%	0.7%	1.32	0.01	0.31	0.01	27.48	0.36
7	190	0.548	320	2	0.5195		0.705		112.5		2	62.2%		7.0%		27.1%		1.33		0.33		27.23	
8	245	0.078	320	2	0.4691		0.591		102.0		2	72.0%		7.5%		14.5%		1.24		0.15		32.85	
9	245	0.144	140	2	0.4658		0.463		88.8		2	70.0%		7.3%		17.0%		1.24		0.18		31.53	
10	245	0.144	560	2	0.4855		0.523		104.6		2	69.9%		7.2%		17.4%		1.22		0.19		31.26	
11	220	0.548	140	2	0.4413		0.784		139.0		1	62.8%		6.7%		27.0%		1.28		0.32		27.10	
12	220	0.548	560	2	0.4035		0.848		186.7		2	70.0%		7.0%		18.8%		1.19		0.20		30.91	
13	245	0.548	320	2	0.3854		0.839		168.5		2	72.1%		7.4%		16.0%		1.22		0.17		32.44	
Total				28	0.5197	0.02	0.558	0.03	97.3	8.0	29	64.6%	1.0%	7.1%	0.0%	23.8%	1.1%	1.32	0.02	0.28	0.02	28.65	0.51

C H O values based on ash free dry weight (AFDW).
T_p process temperature, X concentration of citric acid, d_R retention time, N number of corresponding data sets, A arithmetic mean, σ_N standard error, Y_s hydrochar yield (dry mass), Y_ℓ liquid product phase yield (liquids after HTC – liquids before HTC), Y_g gas yield, g_{DM} gram dry mass crystalline citric acid + dry mass digestate, $g_{DG,DM}$ dry mass digestate, g_{CA} gram citric acid
a Calculated after Mott and Spooner [33].

3.2.3 Product processing

After venting, the amount of product gas was recorded in millilitre and the sampling container was removed for further analytics of the gas composition (in triplicate) with help of a gas chromatograph of Inficon (Type Inficon 3000 µ—GC). For the calculation of the applicable gas density, the current ambient temperature and pressure were recorded for later mass calculations. Then the cover plate of the batch was removed and the autoclave was weighted, containing the hydrochar slurry.

The hydrochar slurry was subjected to a solid-liquid separation using a centrifuge of Hermle (Type Z306-4.500 rpm). The decanted liquid was weighted and frozen to prevent secondary reactions and for further analyses. The solid phase was weighted as well, dried in an oven at 40 °C to its weight balance, milled, packaged and frozen for further analytics.

3.2.4 Analytics

For the dried digestate and solid phase after HTC, the DM content (DIN EN 13040), the bulk density (DIN EN 13041), ignition loss (DIN EN 13039), pH value (DIN EN 13037), elemental composition (DIN EN 15104, 15178), ICP-OES (DIN EN ISO 11885) and higher heating values (DIN 51900) were analysed.

The liquid product phase became subject to the following analyses: pH value (DIN EN 13037), ICP-OES (DIN EN ISO 11885), thermal catalytic oxidation (DIN EN 15936, DIN EN 12260, DIN EN 1484), ion exchange chromatography (DIN EN ISO 10304,DIN EN ISO 14911), high-performance liquid chromatography (DIN 10751–3) and phenol index (DIN EN ISO 14402). The results from these analyses are partially shown in Tab 3.1.

3.2.5 Severity parameters and statistics

3.2.5.1 Process severity

Severity factors have been developed as a way for comparing results among experiments carried out under different conditions and to better understand the underlying reaction kinetics

[20]. In the context of hydrothermal processing of biomass, such severity factors have been developed/applied by a number of different authors [13, 21–26]. Ruyter [21] developed a corresponding coalification model (Eq. 3.1) based on data with a wide range of reaction temperatures (120–390 °C) and retention times (1 min to 6 months). The aim was to predict the degree of carbonization on the basis of biomass properties and reaction conditions. Funke and Ziegler [27] proposed to apply this model for hydrothermal carbonization. Kruse et al. [24] applied this model successfully for the prediction of the carbonization degree for draff as a feedstock and described the underlying reaction kinetics. Kieseler et al. [25] used this severity model to classify data from hydrothermal carbonization of poplar, straw and grass to set up an ultimate prediction model for the HHV of hydrochar.

Eq. 3.1: $$ƒ = 50 \times t^{0.2} \times exp\left(\frac{-3.500}{T}\right)$$

A more complex and generalized severity model for the reaction kinetics of lignocellulosic biomass was developed by Abatzoglou et al. [22]. This model (Eq. 3.2) also considers the acidic and catalytic parameters.

Eq. 3.2: $$ƒ = \int_0^t \exp\left(\frac{X-X_{ref}}{\lambda X_{ref}}\right) \times \exp\left(\frac{T_p-T_{P,ref}}{\omega}\right) \delta d_R$$

Notably, Eqs. 3.1 and 3.2 follow different approaches to describe the influence of the reaction temperature and time on the process severity. This is due to the fact that Ruyter [21] developed his model based on an Arrhenius relation whereas Abatzoglou et al. [22] followed a Taylor series expansion, leading to these different descriptions. Janga et al. [23] applied Eq. 3.2 to predict the yield of monosaccharides after the hydrolysis of soft- and hardwood by concentrated sulfuric acid. For this, the authors assumed the reactions to be isothermal. Subsequently, Eq. 3.2 can be simplified and used in adjusted form (Eq. 3.3). According to Ruiz et al. [20], isothermal reaction conditions can be assumed, when the temperature profile of the experiments follows a specific pattern (see Fig. 3.1).

Eq. 3.3: $$ƒ = \exp\left(\frac{X-X_{ref}}{\lambda X_{ref}}\right) \times \exp\left(\frac{T_p-T_{P,ref}}{\omega}\right) \times d_R$$

For the paper at hand, the parameters X and X_{ref} describe the initial crystalline concentration of citric acid in gram per gram digestate (DM) and the corresponding reference concentration. T_p and $T_{p,ref}$ describe the process temperature and the corresponding reference temperature in degree Celsius. Janga et al. [23] and Montane et al. [28] report that these reference conditions do have an insignificant influence on the results of the severity analysis and the optimal model parameters. The reference values were therefore selected under the premise that the calculated severity parameters would be in a workable number range ($T_{p,ref}$=190 °C; X_{ref}=0.548 g per g digestate). Moreover, λ is a parameter describing the catalytic effect by acids throughout the experiments and ω describes the effect of temperature. To be able to calculate the process severity, both of these parameters must be estimated from the experimental data as described below. The variable d_R is the experiments' duration in minutes as described previously (see Section 3.2.2.2) which marks the influence of the retention time.

3.2.5.2 Yield modelling

It is assumed that the severity models described above can also be used for the prediction of the product mass balance of hydrothermal carbonization of digestate (yield of solid, liquid and gas phase). This assumption will be proven by statistical analysis in Section 3.3. From a visual inspection, it can be anticipated that the data sets follow a logarithmic principle. The general behaviour of the different product phase yields (Y) with respect to the reaction severity is therefore assumed to follow the pattern of Eq. 3.4.

Eq. 3.4: $$Y = c \times \ln(f) + d$$

That this assumption is appropriate will also be proven by statistical analysis in Section 3.1. For the estimation of the parameters λ and ω, Eq. 3.3 needs to be inserted into Eq. 3.4. Further, the following simplifications are applied:

Eq. 3.5: $$u = \frac{X - X_{ref}}{X_{ref}}$$

Eq. 3.6: $$v = T_p - T_{P,ref}$$

Applying Eqs. 3.5 and 3.6 and other simplifications leads to

Eq. 3.7: $$Y = u\frac{c}{\lambda} + v\frac{c}{\omega} + \ln(d_R) \times c\,.$$

To achieve a linear equation, the following substitutions need to be made:

Eq. 3.8: $$w = \ln(d_R)$$

Eq. 3.9: $$a = \frac{c}{\lambda}$$

Eq. 3.10: $$b = \frac{c}{\omega}$$

Inserting Eqs. 3.8, 3.9 and 3.10 into Eq. 3.7 leads to the linear expression for Y with a, b, c and d as regression parameters presented in Eq. 3.11. Equation 3.11 is a mathematical workaround that allows the calculation of the parameters λ and ω by linear curve fit. Although it has a linear form, the incorporated simplifications from Eqs. 3.5, 3.6 and 3.8 assure that it is in fact not linear.

Eq. 3.11: $$Y = au + bv + cw + d$$

The values for u, v and w can then directly be calculated from the process parameters achieved. After linear curve fit based on the yield data in Table 1, λ and ω can be calculated by Eqs. 3.9 and 3.10 from a, b and c. Equation 3.3 is then used for the calculation of the corresponding reaction severities f. Although c and d have already been estimated by this procedure, an additional logarithmic curve fit based on f can now be done to improve the prediction models (Eq. 3.4).

3.2.5.3 Statistical analysis

For all statistical calculations, the software IBM® SPSS Statistics (Version 20) was used. The methodologies applied were spike and correlation analysis (including tests of significance), linear regression, logarithmic curve fit and arithmetic mean analysis. To further assess the quality of the statistical models calculated the average bias error (ABE) and the average absolute error (AAE) according to Eqs. 3.12 and 3.13 have been used:

Eq. 3.12: $$\mathrm{ABE} = \frac{1}{n}\sum_{i=1}^{n}\frac{Y_i^{calc}-Y_i^{exp}}{Y_i^{exp}}$$

Eq. 3.13: $$\mathrm{AAE} = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{Y_i^{calc}-Y_i^{exp}}{Y_i^{exp}}\right|$$

Within Eqs. 3.12 and 3.13, n describes the total number of data sets applied, Y_i^{calc} the predicted model value for data set i and Y_i^{exp} the corresponding experienced (measured) value.

3.3 Results and discussion

3.3.1 Modelling product phase yields and the degree of carbonization

From the 30 experiments carried out, the mass balance results of two runs (runs 6 and 13) were deleted from the raw data due to inconsistencies within the experimental protocol. Afterwards, a spike analysis was done to the raw data. It was found that the results of the elemental composition of the solid product phase from run 20 outranged the other data. The corresponding and relevant box plots are depicted in Fig. 3.2. These results were therefore also deleted from the raw data set. Data sets with the same severity parameters were averaged by means of arithmetical mean, and the data was transformed to a generalized form (see Tab. 3.1).

With help of Tab. 3.1, λ and ω were estimated as described above. The results are shown in Tab. 3.2. Based on Tab. 3.1, the severity parameter f for all product phases were calculated by Eq. 3.3. The assumption that the product yields follow a logarithmic function was tested by a significance test. Based on a 0.01 probability level, all product phase yields showed a significant correlation with the corresponding severity factors (see Tab. 3.2). The corrected coefficients of determination (B_{cor}) calculated range from 0.869 (Y_s) to 0.935 (Y_g) and are consistently lower than the origin values of B. However, the coefficients of correlation (R) are even higher and range from 0.949 (Y_s) to 0.975 (Y_g). To also check the prediction quality of the calculated models for all product phases and for the variety of process conditions applied, the models have been used to calculate the product yields (Y_i^{calc}). ABE and AAE according to

Eqs. 3.12 and 3.13 were calculated then. The corresponding values for ABE range from 0.3 % (Y_s) and 1.7 % (Y_g), whereas the values for AAE range from 4.3 % (Y_s) to 8.4 % (Y_g) (see Tab. 3.2). The models are also depicted in Figs. 3.3, 3.4 and 3.5. The axes of abscissae were logarithmised for better visualization. The figures also include the model equations derived from Eq. 3.4.

Tab. 3.2: Results from the linear curve fit, calculation of λ and ω, and data from statistical analysis (Y_s = hydrochar yield (dry mass); Y_ℓ = liquid product phase yield; Y_g = gas yield).

	Y_s	Y_ℓ	Y_g	H/C	O/C
a	-.144	.418	98.705	-.106	-.044
b	-.003	.002	1.040	-.004	-.004
c	-.019	.043	16.316	-.046	-.056
d	.622	.478	27.911	1.621	.689
λ	.130	.103	.165	.432	1.294
ω	7.210	18.976	15.685	12.579	14.361
R	.949*	.974*	.975*	.961*	.957*
B	.901	.948	.951	.924	.916
B_{cor}	.869	.931	.935	.899	.888
ABE	0.3%	0.47%	0.7%	0.0%	1.1%
AAE	4.3%	6.1%	9.4%	1.5%	10.6%

The variables a, b, c and d are regression parameters from Eq. 3.11. Ys hydrochar yield (dry mass), Y_ℓ liquid product phase yield (liquids after HTC - liquids before HTC), Y_g gas yield, R coefficient of correlation, B coefficient of determination
*Correlation is significant based on a probability of 0.01

Additional cross-checks with the severity model of Ruyter [21] and different underlying functionalities (linear, square and exponential) for the Eq. 3.4 showed that also here a logarithmic functionality is the dominant principle. In 11 of 15 regression analyses, the logarithmic functionality showed best results with regard to correlation and significance. In four cases a square curve fit was slightly better than a logarithmic function. For these cross-checks, Eq. 3.1 was used instead of Eq. 3.3 within the procedure described in Section 3.2.5.2. It can be summarized that the assumed logarithmic principle from Eq. 3.4 is the statistically most significant for the description of the mass yields in HTC.

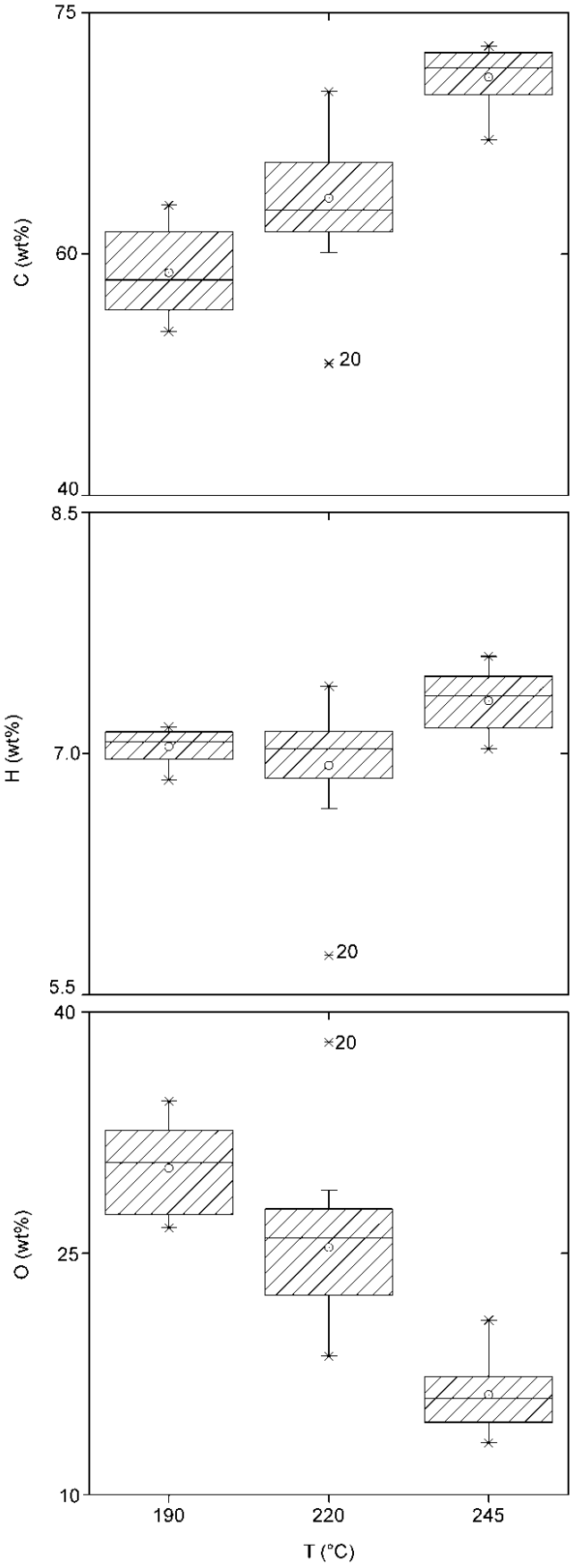

Fig. 3.2: Box-plots from the spike-analysis for carbon, hydrogen, and oxygen content of the hydrochar - Run 20 was found to outrange the other elemental composition data.

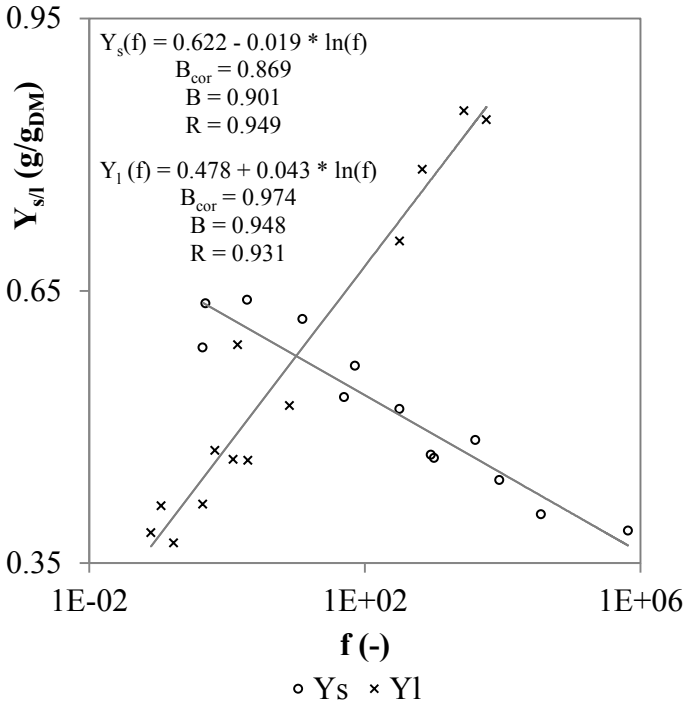

Fig. 3.3: Logarithmic curve fit according to Eq. 3.4 for the solid (Y_s) and liquid (Y_ℓ) product phase yields.

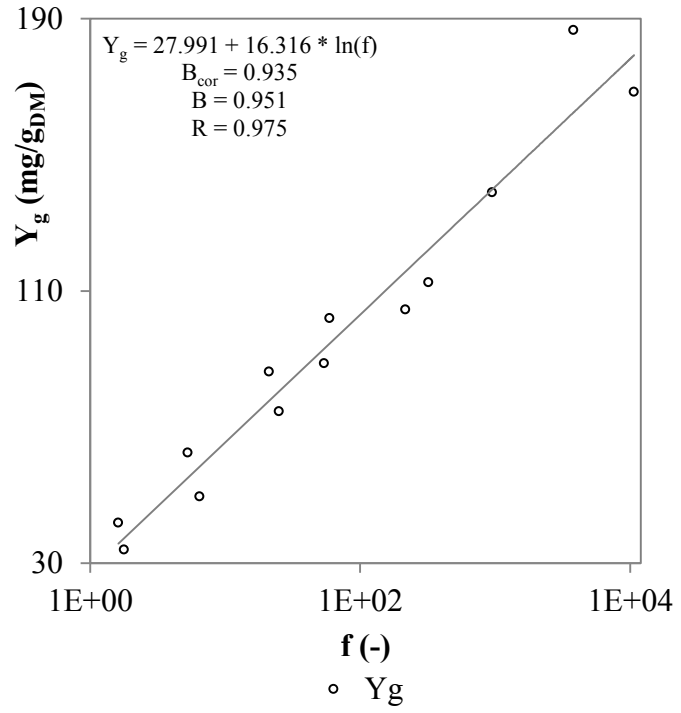

Fig. 3.4: Logarithmic curve fit according to Eq. 3.4 for the gaseous (Y_g) product phase yield.

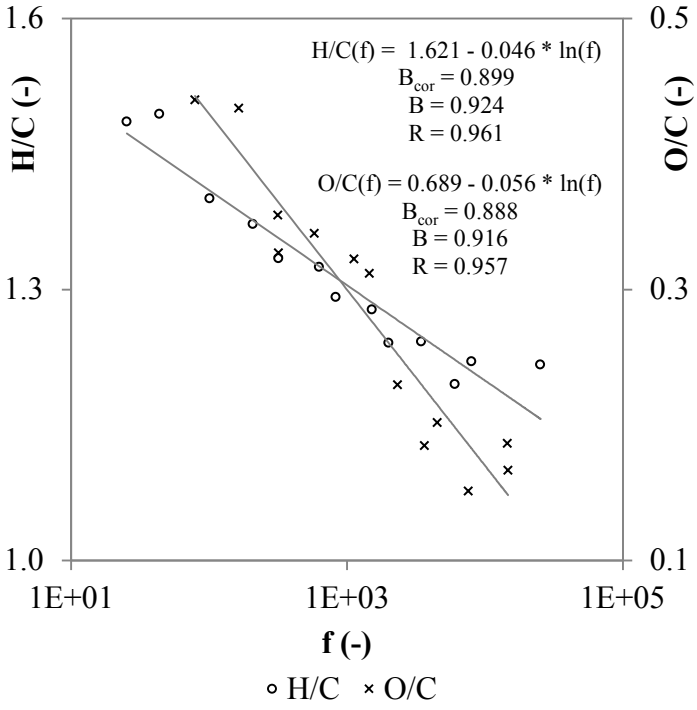

Fig. 3.5: Logarithmic curve fit according to Eq. 3.4 for the H/C and O/C ratios of the hydrochar.

3.3.2 Comparison of the severity patterns

Based on the elemental ratios of H/C and O/C given (Tab. 3.1) a Van-Krevelen Diagram (Fig. 3.6) was set-up and the plotted points were numbered (rank ordered) by increasing severity (1=lowest severity, 13=highest severity) of the O/C ratio (decarboxylation). Within the corresponding inscription of Fig. 3.6 (in parenthesis), also the rank order of the severity parameters of the corresponding product phase yields are depicted (f_s, f_ℓ, f_g). It can be seen that the mass yields follow a different rank order than the decarboxylation. Comparing only the rank orders of the product phase yields (Y_s, Y_ℓ, Y_g) shows little deviations. It can be concluded that the process severity of the O/C (and also H/C) ratio follows a different pattern than that of the corresponding mass yields.

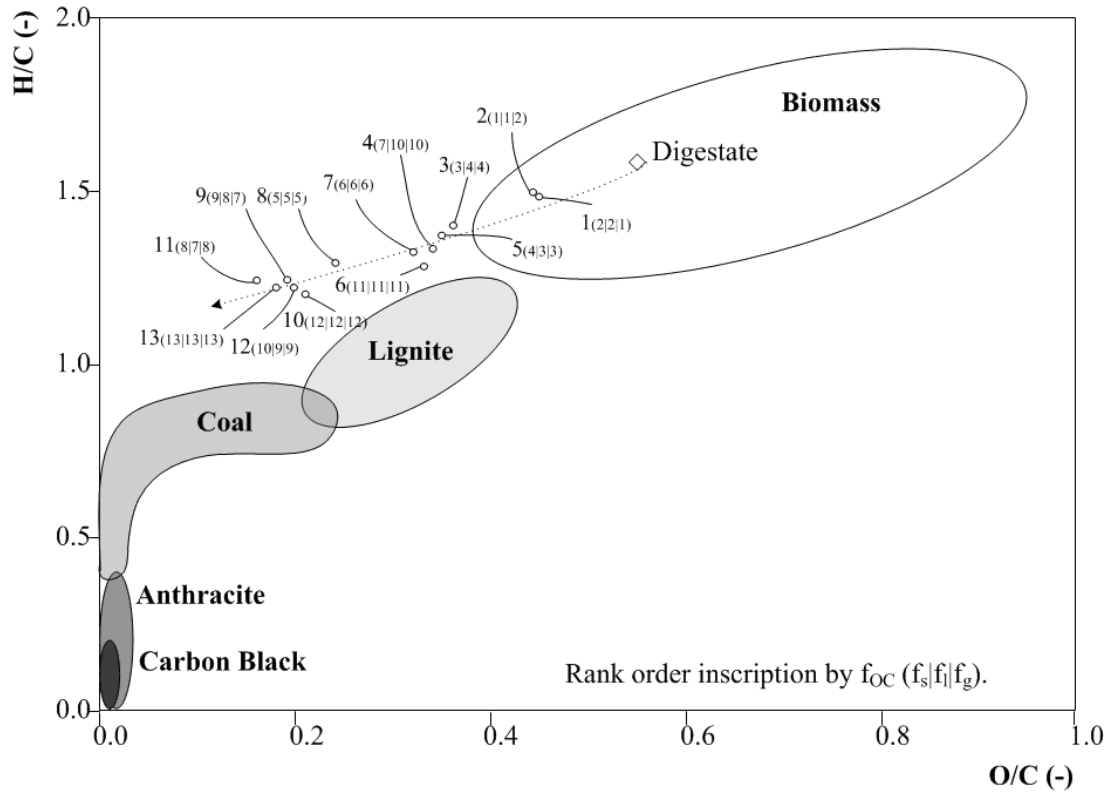

Fig. 3.6: Van-Krevelen Diagram for the HTC of biogas digestate, showing the carbonization pathway and the order of the corresponding product phase yields (rank order inscription: f_{OC} (f_s; f_ℓ; f_g) from lowest to highest (1-13)).

3.3.3 Discussion and sensitivity analysis

It has been shown that modelling by severity can be used for the prediction of the product phase mass yields resulting from hydrothermal carbonization of digestate at varying process conditions. Thereby, all underlying functions are logarithmic. This finding is in contrast to the results of Reza et al. [13] who developed a kinetic model for the hydrochar yield from loblolly pine based on exponential equations. However, the authors applied a limited range of retention times between 15 s and 30 min. Further, they neither used a severity approach nor was the influence of a catalyst on the hydrochar yield examined. In contrast, the approach presented here can also be applied to predict the degree of carbonization for the hydrochar produced. The statistical assessment of our models showed high significance and accuracy in R and ABE.

The comparison of the rank order of the different severity parameters calculated showed that the hydrochar yield decreases with increasing process severity. Gas yield and the yield of

liquid products increase. This is in accordance with the findings of Hoekman et al. [18] who conducted a series of HTC experiments with a mixed wood feedstock in temperature range between 215 and 295 °C. Nevertheless, the degree of carbonization does (based on the corresponding severity parameters) not follow the same pattern as the mass yields.

From the literature, it is qualitatively known that temperature, retention time, acidity, particle size, water content of the feedstock and the presence of ionic salts do have influence on the HTC reaction and its output [9–19, 24, 29]. Nevertheless, temperature was found to have a major impact compared to the other factors [2, 9, 12, 16, 17, 19, 29, 30]. Apart from that, no publication was found that really described the difference in impact mathematically. Therefore, this aspect is analysed in more detail in the following.

Accordingly, we combined Eqs. 3.3 and 3.4 for a sensitivity analysis. This led to numerical expressions for the impact of changing process parameters on the corresponding product phase yields. The following general equations are derived from this procedure:

Eq. 3.14: $$\frac{\partial \mathrm{Y}}{\partial X} = \frac{\mathrm{c}}{\lambda X_{ref}}$$

Eq. 3.15: $$\frac{\partial \mathrm{Y}}{\partial T_p} = \frac{\mathrm{c}}{\omega}$$

Eq. 3.16: $$\frac{\partial \mathrm{Y}}{\partial d_R} = \frac{\mathrm{c}}{\mathrm{d}_R}$$

While Eqs. 3.14 and 3.15 describe a constant impact rate for a change in X and T_p, the impact by d_R (Eq. 3.16) decreases with an increasing retention time. Inserting the parameters from Tab. 3.2 into these equations leads to the impact matrix shown in Tab. 3.3. As the impact values in Tab. 3.3 describe, e.g. the change in mass yield per unit (e.g. per additional gram citric acid, degree Celsius and/or retention time in minutes), they are not directly comparable to each other. For better comparison, they should be set into the context of the experimental set-up. In this respect, Tab. 3.4 describes a 10 % parameter change based on the centre point (T_p=220 °C | X=0.144 g_{CA}/g_{DM} | d_R= 320 min) of our experimental set up using Eqs. 3.14, 3.15 and 3.16.

Tab. 3.3: Impact matrix for the quantitative impact of general parameter change (T_p; X; d_R) on product yields and degree of carbonization.

		δY_s (g_s/g_{DM})	δY_ℓ ($g_l/g_{DG,DM}$)	δY_g (mg/g_{DM})	δH/C (-)	δO/C (-)
δX	(g_{CA}/g_{DM})	-2.63E-01	7.63E-01	1.80E+02	-1.93E-01	-7.95E-02
δT_p	(°C)	-2.61E-03	2.28E-03	1.04E+00	-3.64E-03	-3.93E-03
δd_R	(140 min)	-1.35E-04	3.08E-04	1.17E-01	-3.27E-04	-4.03E-04
	(320 min)	-5.88E-05	1.35E-04	5.10E-02	-1.43E-04	-1.76E-04
	(560 min)	-3.36E-05	7.71E-05	2.91E-02	-8.18E-05	-1.01E-04

From Tab. 3.4, it can be seen that a 10% increase in process temperature (δT_p=22 °C) in HTC of biogas digestate has by far the highest impact on the product phase yields and the carbonization of the hydrochar (measured by decreasing H/C and O/C ratios) when compared to the impact of a similar change in citric acid concentration and retention time. The effect of a similar increase in citric acid concentration (δX= 0.0144 g_{CA}/g_{DM}) only makes 6.6 % of the impact of a changed temperature. Retention time (δd_R=32 min) only makes 3.2 % of this impact and is therefore half as large as the impact of increased citric acid concentration. Notably, the behaviour of the H/C and the O/C ratios differs from the behaviour Y_s. The numbers show that an increase in d_R has a stronger influence on the degree of carbonization than an increase in X. For Y_s, Y_ℓ and Y_g, this finding applies inversely and may explain the difference in the severity rank orders described in Section 3.3.2.

Tab. 3.4: Impact matrix for the HTC of biogas digestate for a 10 % parameter increase, starting from the experimental center point at T_p = 220°C, X = 0.144 g_{CA}/g_{DM}, and d_R = 320 min.

	δY_s (g_s/g_{DM})	δY_ℓ ($g_l/g_{DG,DM}$)	δY_g (mg/g_{DM})	δH/C (-)	δO/C (-)
δX = 0,0144 g_{CA}/g_{DM}	- 0.004	0.011	2.592	- 0.003	- 0.001
δT_p = 22 °C	- 0.057	0.050	22.885	- 0.080	- 0.086
δd_R = 32 min	- 0.002	0.004	1.555	- 0.004	- 0.005

3.4 Conclusions

It has been shown that modelling by severity can be used for the prediction of the product phase mass yields of hydrothermal carbonization of digestate under varying process conditions. All underlying prediction models significantly follow a logarithmic approach. The

same procedure can be used to predict the degree of carbonization of the hydrochar produced. Further research is needed to strengthen the database for the prediction models presented and to extent this kind of statistical-based mass balancing to the HTC of other biomass.

Although quantitative comparisons of the impact of different process parameters were done previously [31, 32], for the first time the impact of different process parameters was calculated for HTC of biogas digestate based on statistical models. It was found that temperature is by far the dominant impact factor for product mass yields and carbonization. The citric acid concentration has the second best impact on product phase mass yields followed by retention time. With respect to the degree of carbonization, citric acid concentration and retention time change their impact order. This fact emerges in a different severity rank order for the mass yields on the one hand and the O/C and H/C ratios on the other. Further research is needed to examine and mathematically describe the possible impact on mass balance and degree of carbonization by particle size, dry mass to water ratio and the presence of ionic salts in the feedstock.

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SECTION 4

HYDROTHERMAL CARBONIZATION OF WHEAT STRAW – PREDICTION OF PRODUCT MASS YIELDS AND DEGREE OF CARBONIZATION BY SEVERITY PARAMETER[4]

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4. HYDROTHERMAL CARBONIZATION OF WHEAT STRAW – PREDICTION OF PRODUCT MASS YIELDS AND DEGREE OF CARBONIZATION BY SEVERITY PARAMETER

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Abstract

The product yields of hydrothermal carbonization of wheat straw as well as the degree of carbonization are quantified as functions of process parameters by using a severity approach. The process severity was calculated from temperature, retention time and catalyst concentration. Data gained from batch experiments (190-245 °C, 150-570 min) were used to fit the model parameters. By these models basing on few selected reaction conditions a wide range of process conditions can be covered and the yields for the solid, solved organic, and gaseous product phase can be predicted. Moreover, the paper delivers model equations for the prediction of the H/C and O/C ratios for the solid product phase. Such model equations can be used for process optimization and for valid LCA calculations.

Keywords

hydrothermal carbonization, wheat straw, severity parameter, model equations, mass balance, degree of carbonization, hydrochar

4.1 Introduction

Research on hydrothermal carbonization (HTC) was started in the early 20th century by Bergius who mimicked natural coalification processes by biomass conversion at high pressure and temperature [1]. In recent years HTC regained attention and a lot of valuable research has been done in the recent years on hydrothermal carbonization (HTC). The scope was and is on the impact of reaction parameters (e.g. process temperature, retention time, acid concentration, particle size of the biomass, dry mass to water ratio in the feedstock) to the outcome of the process [2–12].

Severity factors have been developed and applied before with respect to hydrothermal processing of biomass [6, 13–18]. Ruyter [13] for example developed a general coalification model based on a wide-ranged data set considering temperatures and retention times. Funke and Ziegler [19] proposed to apply this model on HTC. Kruse et al. [16] used a modified model equation to predict the degree of carbonization degree of draff. Kieseler et al. [17] used this model for the classification of data from HTC of different biomass and for the set-up of a prediction model for the higher heating value (HHV) of hydrochar. Abatzoglou et al. [14] developed a more complex severity model than Ruyter for the reaction kinetics of lignin-rich biomass. Janga et al. [15] applied this model for the prediction of the monosaccharides yield via hydrolysis of different wood by concentrated sulfuric acid. Suwelack et al. [20] applied this severity model to predict the gaseous, liquid, and solid mass yield as well as the degree of carbonization for the HTC of biogas digestate. The authors developed mathematical model equations for the description of mass balances (based on the variation of temperature, retention time and citric acid concentration) that can be used for e.g. Life-Cycle-Assessment (LCA) and optimization of the HTC process.

This paper transfers the approach presented by Suwelack et al. [20] to corresponding experimental data for wheat straw. The prediction of mass yields and the degree of

carbonization by severity parameter as function of varying process conditions will be achieved this way.

4.2 Materials and Methods

Below, materials, equipment, and analytic methods are described. All experiments are carried out with milled wheat straw.

4.2.1 Materials

The biomass used was wheat straw from a farm close to Karlsruhe (Germany). In order be able to produce a homogeneous reactant slurry for the experiments, the straw was milled (≤ 5 mm) and sieved. The fraction between 1 and 2 mm was used for the experiments. This straw dust was spread evenly in an oven and dried at 40 °C to constant weight. The dry mass (DM) content (ξ_{WS}) was determined with three samples (ξ_{WS} = 92.67 wt%; N = 3; σ_N = 0.14 wt%) by determination of the weight difference before and after drying. Afterwards it was stored under dry conditions in a closed container.

4.2.2 Experimental set-up

4.2.2.1 Citric Acid

In contrast to Suwelack et al. [20] there was no need to estimate the buffering capacity of the reactant suspension due to the fact that deionized water was used instead of a biologically active liquid phase (liquid digestate). However, the buffering capacity of the suspension (including the straw) was tested by 2-molar citric acid solution and continuous 'pH Stat' titration. The pH value of the solution initially was 7 and it changed immediately and permanent when the acid solution was added. No pH variation was observed while the suspension was stirred and monitored for several hours. From further titration experiments it was known that the following additions of crystalline citric acid are needed and applied here to sustainably change the pH value: 1.7 mg (pH 5), and 20 mg (pH 3) citric acid per g wheat straw dry mass.

4.2.2.2 Carbonization experiments

For the carbonization experiments the same experimental set-up and autoclaves were used as described by Suwelack et al. [20]. Cylindrical 250 ml batch autoclave (h = 110 mm, d = 74 mm) made from stainless steel (1.4571), equipped with internal sensors for pressure and temperature were applied. The process temperature (T_p) was 190, 220, and 245 °C. In contrast to the publication mentioned above, the experiments were carried out for reaction times of 150, 330 and 570 minutes (d_R). Dried wheat straw was mixed with deionized water to a total extent of 15 wt% DM of straw directly in the batch. The mixture was homogenized by stirring and crystalline citric acid was added. As described above the initial additive (citric acid) concentrations (X) were zero, 1.7 and 20 mg per g wheat straw (DM). Reaction time was measured from the point the reactors reached 180°C. Heating was done in a repurposed gas chromatograph oven at constant temperature.

Box-Behnken experimental design was also applied to reduce the number of runs to 15 including 3 runs for the Centre Point (CP) [12, 20]. Every experiment was repeated once, so that totally 30 experiments were carried out in random order. The different set-ups are illustrated in Tab. 4.1.

At the end of the desired reaction time the batch reactor was cooled down to ambient temperature conditions by water quenching for 20 minutes. After that, the autoclave was diligently dried outside with a clean towel and connected to a gasometer. A gas sample was taken to analyse the gas composition.

Tab. 4.1: Experimental set-up and results from the HTC of wheat straw: mass balances, elemental composition of the hydrochar, and energy content.

No.	T_R [°C]	X [mg_{CA}/$g_{ws,DM}$]	d_R [min]	N	Y_s [$g_{s,DM}/g_{DM}$]		N	Y_ℓ [$g_\ell/g_{ws,DM}$]		N	Y_g [mg/g_{DM}]		N	C		N	H		N	O		H/C		O/C		N	HHV[1] [MJ/kg]	
					A	σ_N		A	σ_N		A	σ_N		A	σ_N		A	σ_N		A	σ_N	A	σ_N	A	σ_N		A	σ_N
1	190	20	330	2	.691		2	.236		2	30.5		2	54.2%		2	6.2%		2	38.6%		1.36		0.54		2	22.10	
2	245	20	330	2	.430		2	.359		2	145.7		2	71.9%		2	5.8%		2	20.7%		0.96		0.22		2	29.50	
3	190	0	330	2	.830		1	.166		2	35.1		1	55.6%		2	6.0%		1	37.4%		1.20		0.51		1	21.91	
4	245	0	330	2	.433		2	.381		2	121.2		2	75.7%		2	6.0%		2	16.6%		0.95		0.16		2	31.66	
5	190	1.7	150	2	.783		2	.186		2	26.9		1	54.9%		2	6.5%		1	37.5%		1.40		0.51		1	22.85	
6	245	1.7	150	1	.446		2	.327		2	120.6		2	71.2%		2	6.1%		2	21.1%		1.02		0.22		2	29.63	
7	190	1.7	570	2	.794		2	.144		2	38.2		2	55.0%		2	6.2%		2	37.7%		1.36		0.52		2	22.56	
8	245	1.7	570	2	.461		2	.333		2	131.8		2	72.9%		2	6.1%		2	19.4%		1.00		0.20		2	30.47	
9	220	20	150	2	.648		2	.303		2	73.6		2	60.1%		2	6.3%		2	32.5%		1.25		0.41		2	24.88	
10	220	0	150	2	.688		2	.191		1	67.5		2	59.7%		1	6.4%		2	33.0%		1.23		0.42		1	24.40	
11	220	20	570	2	.561		2	.255		2	79.3		2	69.6%		2	6.1%		2	22.8%		1.05		0.25		2	28.98	
12	220	0	570	2	.547		2	.272		2	108.2		2	70.7%		1	6.2%		2	21.9%		1.00		0.24		1	29.37	
13	220	1.7	330	6	.592	.031	6	.270	.040	6	88.3	16.7	6	64.1%	0.7%	6	6.1%	0.1%	6	28.4%	0.8%	1.14	.005	0.33	.015	6	26.48	.42
Total				29	.611	.131	29	.268	.080	29	83.4	39.2	28	64.9%	7.1%	28	6.1%	0.2%	28	27.6%	7.3%	1.13	.146	0.33	.125	26	26.81	3.20

[1] Calculated after Mott and Spooner [21].

T_p = process temperature; X = concentration of citric acid; d_R = retention time; N = number of corresponding data sets; A = arithmetic mean; σ_N = standard error

Y_s = hydrochar yield (dry mass); Y_ℓ = process water yield = process water after HTC – process water before HTC; Y_g = gas yield

g_{DM} = g dry mass = crystalline citric acid + wheat straw dry mass; $g_{WS,DM}$ = dry mass wheat straw; g_{CA} = g citric acid

C H O values based on ash free dry weight (AFDW).

4.2.3 Product processing and analytics

After venting, the amount of product gas was recorded in milliliter. Pressure and temperature in the laboratory are measured to calculate the product gas density. The weight difference compared to start of the experiment was determined. The hydrochar slurry was subjected to a solid-liquid separation as described by Suwelack et al. [20] in more detail. The solid phase was weighted, dried until constant weight is reached at 40 °C, milled, packaged and frozen for further analytics. The further processing and analytics of solids and liquids is illustrated in Tab. 4.2. The results from these analyses are partially shown in Tab. 4.1.

Tab. 4.2: Analytics applied to solid and liquid product phases from HTC of wheat straw.

Analytics	**Standard applied**	**Applied to**
dry mass content	DIN EN 13040	ws s
bulk density	DIN EN 13041	ws, s
ignition loss	DIN EN 13039	ws, s
pH value	DIN EN 13037	ws, s, ℓ
elemental composition	DIN EN 15104, 15178	ws, s
ICP-OES	DIN EN ISO 11885	ws, s, ℓ
higher heating value	DIN 51900	ws, s
thermal catalytic oxidation	DIN EN 15936, DIN EN 12260, DIN EN 1484	ℓ
ion exchange chromatography	DIN EN ISO 10304, DIN EN ISO 14911	ℓ
high performance liquid chromatography	DIN 10751-3	ℓ
phenol index	DIN EN ISO 14402	ℓ

ws = wheat straw; s = solids; ℓ = liquids

4.2.4 Process severity and statistical analysis

As described previously severity factors have been developed for comparing results of experiments carried out under different conditions [22]. Beside other approaches Suwelack et al. [20] have used an adjusted severity approach after Abatzoglou et al. [14] to predict gaseous, liquid and solid mass yields from hydrothermal carbonization of biogas digestate (see Eq. 4.1 and 4.2). Additionally the same approach can be used to predict the degree of carbonization of hydrochars in terms of their HC and OC ratios [20].

Eq. 4.1: $$\mathfrak{f} = \exp\left(\frac{X - X_{ref}}{\lambda X_{ref}}\right) \times \exp\left(\frac{T_p - T_{P,ref}}{\omega}\right) \times d_R$$

Within Eq. 4.1 X and X_{ref} describe the initial concentration of crystalline citric acid in g per g wheat straw (DM) and the corresponding reference concentration. T_p and $T_{p,ref}$ describe the process temperature and the corresponding reference temperature in degree Celsius. It has been reported previously [15, 23] that these reference conditions only have an insignificant influence on the results of the severity analysis. The reference values for the analysis within in this paper are therefore selected based on practical considerations ($T_{p,ref}$ = 190 °C; X_{ref} = 20 mg per g dry mass wheat straw). The variable d_R is the experiments' the experiments' retention time in minutes. Moreover λ is a parameter describing the catalytic effect by acids throughout the experiments and ω describes the effect of temperature.

Following Suwelack et al. [20] the underlying equation for the prediction of the corresponding yields or carbonization degree is logarithmic (Eq. 4.2). This is in contrast to the findings of other authors [6].

Eq. 4.2: $$Y = a \times \ln(f) + b$$

However, the authors [20] presented a mathematical workaround that allows the calculation of the parameters λ and ω by linear curve fit. Afterwards a and b from Eq. 4.2 can be estimated by logarithmic curve fit. Further details on the approach applied can be found elsewhere [20]. With the equations described above this paper follows the same approach to set-up corresponding prediction models for the HTC of wheat straw.

For all statistical calculations the software IBM® SPSS Statistics (Version 20) was used. To further assess the quality of the statistical models calculated, the Average Bias Error (ABE) and the Average Absolute Error (AAE) have been used (compare [20]).

4.3 Results and discussion

4.3.1 Data and model equations

From 30 experiments carried out, the measured process water yield from one run (Run 5) was deleted from the raw data due to inconsistencies within the experimental protocol. Further, a spike analysis revealed that the solid mass yield of run 12, the carbon and oxygen content of

run 6 and 9, and the hydrogen content of run 19 and 23 of the solid product outranged the other data. This also applied to the measured gas yield of run 19. These results were deleted from the raw data set as well. Data sets with the same severity parameters were averaged by arithmetical mean and the data was transformed to mass specific values (see Tab. 4.1).

Tab. 4.3: Results from the linear curve fit, calculation of λ and ω, and data from statistical analysis (Y_s = hydrochar yield (dry mass); Y_ℓ = liquid product phase yield; Y_g = gas yield).

	Y_s	Y_ℓ	Y_g	H/C	O/C
results from linear curve fit					
λ	1.097	.065	-17.4	-16.9	-5.5
ω	6.535	.787	7.491	15.376	11.573
results from logarithmic curve fit					
a	-.039	.002	13.214	-.097	-.067
b	.980	.188	-44.291	1.892	.901
R	.965*	.919*	.978*	.933*	.964*
B	.932	.845	.957	.871	.930
B_{cor}	.926	.831	.953	.860	.924
ABE	0.4%	1.45%	0.2%	0.2%	1.1%
AAE	5.4%	9.5%	8.0%	3.9%	10.6%

a and b = regression parameters from Eq. 4.2.
R = coefficient of correlation.
B = coefficient of determination.
* Correlation is significant based on a probability of 0.01.

With the data from Tab. 4.1 λ and ω were estimated according to [20]. The results are shown in Tab. 4.3. Based on these values the severity parameters ƒ for all product phases were calculated by Equation 4.1. A correlation analysis showed that the product phase yields (and also the elemental ratios) are significantly correlated with ƒ and ln(ƒ). For all ln(ƒ)-correlations the significance is based on a probability level of 0.01.

Product phase yields and the elemental ratios were then subjected to a logarithmic curve fit with the corresponding values of ƒ as the independent variable. The corrected coefficients of determination (B_{cor}) calculated range from 0.831 (Y_ℓ) to 0.953 (Y_g) and are consistently lower than the origin values of B. However, the coefficients of correlation (R) are even higher and range from 0.919 (Y_ℓ) to 0.978 (Y_g).

The corresponding values for ABE range from 0.2% (Y_g and H/C) and 1.45% (Y_ℓ), whereas the values for AAE range from 3.9 % (H/C) to 10.6 % (O/C) (see Tab. 4.3). The curve progressions and model equations are depicted in Fig. 4.1, 4.2, 4.3, and 4.4. The axes of abscissae were logarithmized for better visualization.

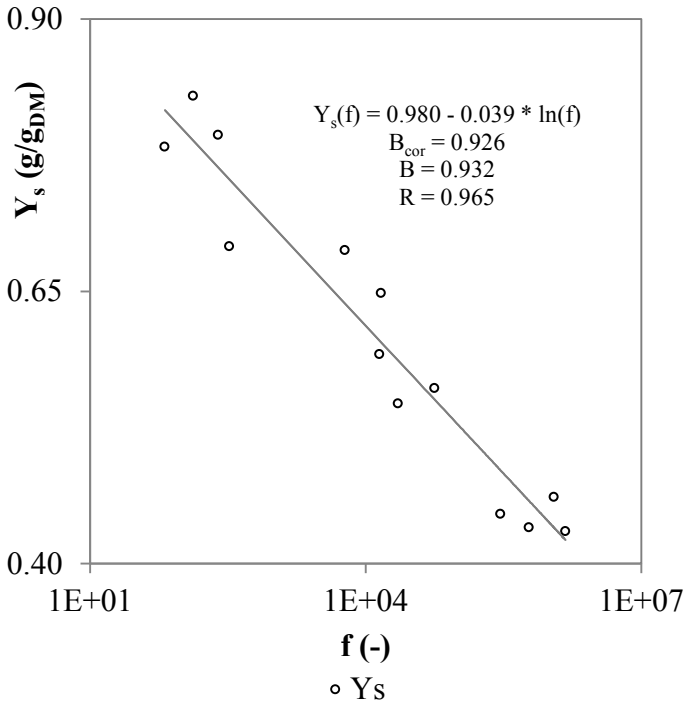

Fig. 4.1: Logarithmic curve fit according to Eq.4.2 for the solid (Y_s) product phase yields.

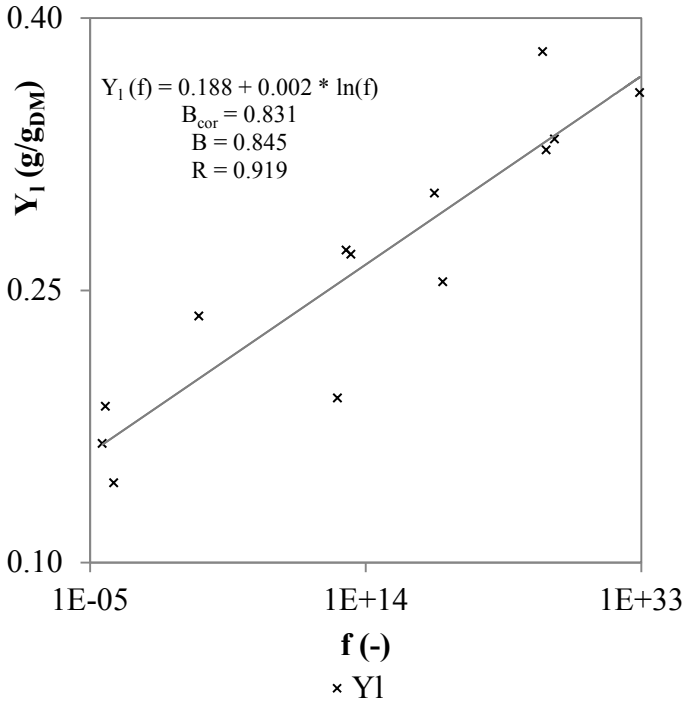

Fig. 4.2: Logarithmic curve fit according to Eq.4.2 for the liquid (Y_ℓ) product phase yields.

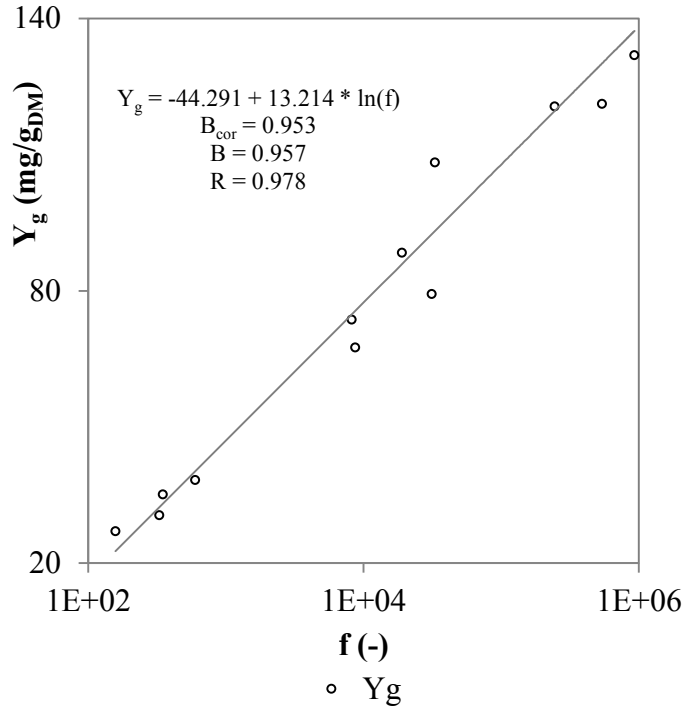

Fig. 4.3: Logarithmic curve fit according to Eq.4.2 for the gaseous (Y_g) product phase yield.

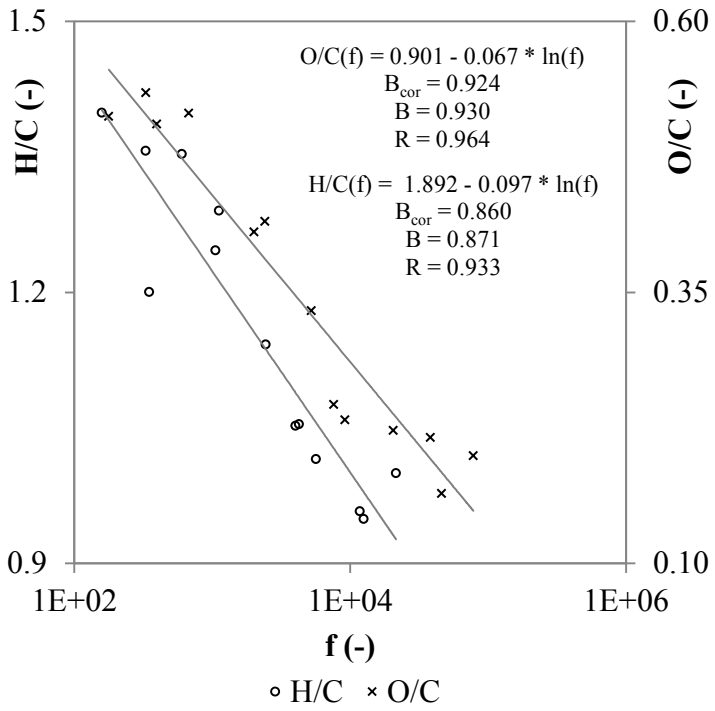

Fig. 4.4: Logarithmic curve fit according to Eq. 4.2 for the H/C and O/C ratios of the hydrochar.

4.3.2 Comparison of the severity patterns

Similar to Suwelack et al. [20] also the rank-ordered severity patterns for all product phases and the carbonization properties were subjected to further investigations. In this respect Fig. 4.5 shows the Van-Krevelen Diagram with the data points plotted and numbered (rank

ordered) by increasing severity (1 = lowest severity; 13 = highest severity). This rank order of the severity parameters is hereby labelled as follows: f_{OC} (f_s; f_ℓ; f_g). Suwelack et al. [20] found that the mass yields for biogas digestate follow a different pattern (rank order) than the H/C and O/C ratios with increasing severity. For the HTC of wheat straw the corresponding patterns are more homogeneous compared to digestate. This finding can be observed by the different rank order numbers in Fig. 4.5. The overall variations between these numbers are lower in the case of wheat straw.

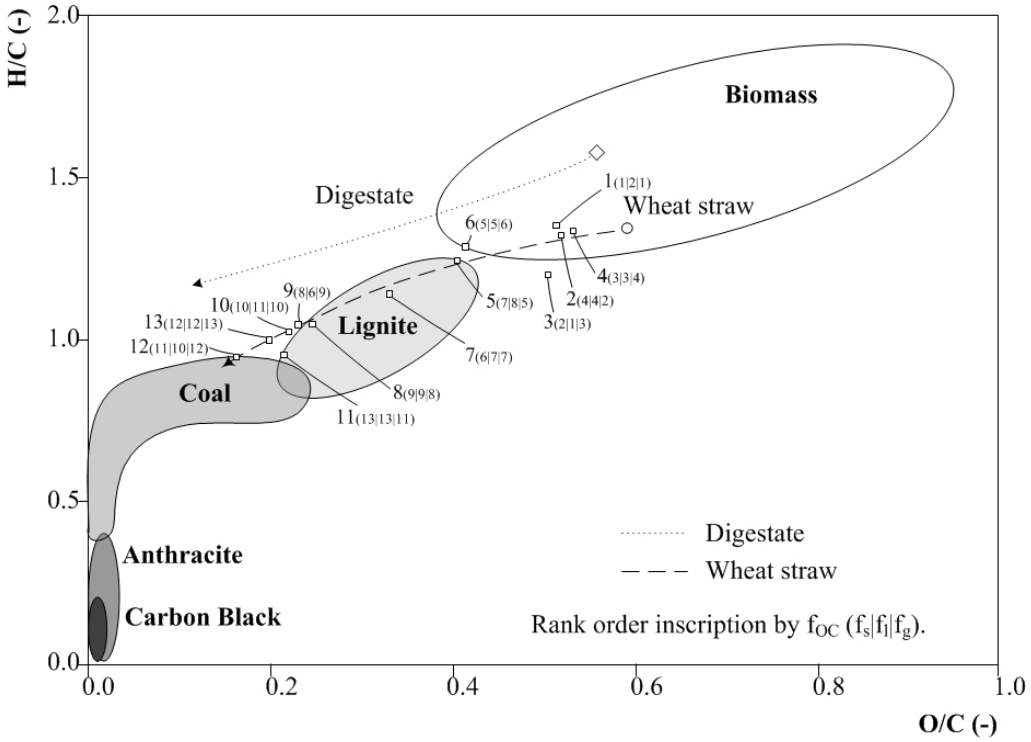

Fig. 4.5: Van-Krevelen Diagram for the HTC of wheat straw, showing the carbonization pathway and the order of the corresponding product phase yields (rank order inscription: f_{OC} (f_s; f_ℓ; f_g) from lowest to highest (1-13)).

4.3.3 Discussion

The results from statistical analysis presented in this work show that the approach of using severity parameters for the prediction of mass yields and carbonization for HTC presented by Suwelack et al. [20] can be transferred to other biomass such as wheat straw. The statistical assessment of our models revealed high significance and accuracy in R and ABE for this kind of biomass as well.

The comparison of rank order of different severity parameters calculated showed that the hydrochar yield decreases with increasing process severity. Gas yield and the yield of liquid products increase. This is in accordance with the results in literature [11, 20].

For better quantitative description the impact of the different process parameters on the outcome of HTC of wheat straw a sensitivity analysis was processed to these models according to Suwelack et al. [20]. In this respect Tab. 4.4 describes a 10 % parameter change based on the centre point (T_p = 220 °C | X = 1.7 mg_{CA}/g_{DM} | d_R = 330 min) of the experimental set-up. In accordance with the findings in literature [2, 5, 9, 10, 12, 24–26] temperature also here was found to have a dominant impact compared to other factors. With the above mentioned increase in temperature, Y_s decreases by 21.9 % while Y_ℓ increases by 25.6 %, and Y_g by 45.2%. Moreover the H/C ratio of the hydrochar decreases by 12.2 % and the O/C ratio by 38.6% (compare Tab. 4.4). Compared to this, a corresponding increase in retention time changed only slightly changed these values. Notably, it seems that the increase in citric acid addition (1.86 mg_{CA}/g_{DM}) did not these yields at all. This might be due to the fact that a 10 % increase in citric acid (based on the centre point) is not able to initiate a sustainable change of the pH value of the reactant slurry. Following our sensitivity analysis, such a change would only incidence the pH value by additionally adding 4.12 mg_{CA} per g_{DM} to the centre point compilation. However, following the model equations also by this modification (compared to the impact of temperature) no reasonable changes in the corresponding mass yields will be achieved.

Tab. 4.4: Impact matrix for the HTC of wheat straw for a 10 % parameter increase, starting from the experimental center point at T_p = 220°C, X = 1.7 mg_{CA} per g_{DM}, and d_R = 330 min.

	δY_s (g_s/g_{DM})	δY_ℓ ($g_\ell/g_{DG,DM}$)	δY_g (mg/g_{DM})	δH/C (-)	δO/C (-)
δX = 0,17 mg_{CA}/g_{DM}	-0.000	0.000	-0.006	0.000	0.000
δT_p = 22 °C	-0.132	0.066	38.809	-0.138	-0.127
δd_R = 33 min	-0.004	0.000	1.259	-0.009	-0.006

More interesting is a comparison of the impact of increased temperature (by 10 %) between wheat straw and biogas digestate [20]. It shows that an increase of 22 °C (starting from the center point) has deeper impact on wheat straw than on digestate. The effect on wheat straw (-0.132 gram hydrochar per gram dry mass) is twice as high (compared to -0.057 gram hydrochar per gram dry mass for digestate). Accordingly the impacts on the mass yields for liquids and gases for wheat straw are also higher and quantitatively point into the opposite direction than the hydrochar yield. It is likely that these observations can be traced back to the higher lignin content and the low content of holocellulose within digestate compared to wheat straw [27, 28]. This observation was also made by Kruse and Grandl [29].

Further, for both wheat straw and biogas digestate [20] the model equations for the O/C ratio follow a decreasing logarithmic principle. In contrast, Reza et al. [6] developed model equations for the prediction of the C and O mass content of the hydrochar for of wheat straw digestate, which follow a power law principle. The equations of Reza et al. can also be used to calculate the O/C ratio (based on molar values) for this kind of biomass, while varying the retention time and the desired process temperature. In this way it reveals that these predicted O/C values also follow a power law principle. Interestingly, it can be found that on each temperature step of this deviated O/C equation, the O/C ratios are increasing with soaring retention time (and therefore with increased process severity). This is inconsistent with the findings presented here and elsewhere [12, 20]. A reason for that might be that the power law curve fit was conducted on four data points each only.

However, the results presented here are also only an example for application of the mathematical methodology developed by Suwelack et al. [19], which should be extended to a much broader variety of different sorts of biomass. A comprehensive and reliable database for HTC yield prediction can be built up this way and used for further process optimization and evaluation. Although wet straw has not the highest importance compared to other fuels and

the experiments presented were carried out under lab conditions as a model case, the results verify and emphasize the broad applicability of the underlying mathematical approach. Whereas the bare equation values in Table 3 can be criticized due to their limitation to the model case presented, it is very likely that the mathematical approach used can also be adapted to other experimental set-ups with e.g. alternating initial dry mass concentrations or different particle sizes. However, this still needs to be proven by further research.

4.4 Conclusions

It has been shown, that the severity approach for the prediction of the product phase mass yields of hydrothermal carbonization of digestate [20] can easily transferred to other biomass, wheat straw in the case presented here. Accordingly, this work presents model equations for the prediction of solid, liquid, and gaseous mass yields and the H/C and O/C ratios of hydrochars. Further research is needed to examine and mathematically describe the possible impact on mass balance and degree of carbonization by particle size, dry mass to water ratio, and the presence of ionic salts in the feedstock.

The sensitivity analysis revealed that temperature for wheat straw as well is by far the dominant impact factor for product mass yields and carbonization. Moreover citric acid addition does not seem to have a reasonable impact on mass yields and carbonization. In direct comparison between wheat straw and biogas digestate it was found that the decrease in hydrochar yield is twice as high for wheat straw compared to biogas digestate. The reason for that seems to be the higher lignin content within the digestate.

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SECTION 5

CONCLUSIONS AND OUTLOOK

5. CONCLUSIONS AND OUTLOOK

Within this work an integrated approach for a *unified appraisal framework* (UAF) for biomass conversion systems was presented (Section 2) [1] and first steps to its application on hydrothermal carbonization were made (Section 3 and 4) [2, 3]. The interplay of the different sections is depicted in Fig. 1.6. From this figure it can be seen, that Section 3 and 4 deliver the necessary input data for proper mass balancing of the HTC technology (with different sorts of biomass), which is needed for the so called *Technology Design Assessment* (TDA) within the Proposed UAF (Section 2).

In this respect **Section 2** describes in detail a new and standardized methodology for the (sustainability) assessment of biomass conversion systems/technologies, which is built-up on TDA (data level) in the first step, followed by life-cycle sustainability assessment (impact level) and finalized by a novel and tailor-made multi-criteria decision making method, called *Multi-criteria Based Benchmarking* (MCBB - decision level). The approach presented can be taken as a first attempt to better integrate existing assessment methods by standardizing the work flow for the appraisal of biomass conversion systems and setting-up guidelines for data gathering and production. Further, it addresses all needs described in literature for this kind of appraisal framework [4] and allows for better examination of the interdependencies of the triple bottom line of sustainability [5]. Further, *Advanced Radar Plots* (ARP) are used to visually illustrate and compare different policy options on the decision making level.

Within **Section 3 and 4** model equations for the prediction of product mass yields of hydrothermal carbonization (as well as the degree of carbonization of the hydrochar) from biogas digestate and wheat straw are quantified by using a severity approach. Data gained from batch experiments was used to fit the model parameters. Using these models basing on few selected reaction conditions, a wide range of process conditions can be covered and the yields for the solid, liquid and gaseous product phase can be predicted. The accuracy of all derived equations was found to be high [2, 3].

It can be concluded, that the research objectives determined in section 1.4.3 have been achieved. Based on this work, a fundamental TDA of HTC for biogas digestate was already set-up and a Life-Cycle-Costing approach was applied. The results of this economic assessment have been presented in the context of an international scientific conference [6]. However, for the complete assessment of HTC and its comparison with other biomass conversion technologies/systems further research on the data and impact level of the proposed approach is needed (compare Fig. 2.1). Specifically for HTC still the environmental and societal impacts need to be quantified on the base of the proposed standardised work flow. For other biomass conversion systems/technologies, e.g. hydrothermal liquefaction and gasification, it is recommended to gather proper mass balance data in literature or experimental research to properly conduct a TDA. This also applies for more mature technologies from other conversion routes.

Before decision making and comparison of different technologies and conversion systems can take place, more research has to be done on category and criteria weighting as well as on criteria selection within MCBB. A Delphi survey with explicit involvement of experts, lay people and potential stakeholders could be an appropriate tool to select right decision criteria and to develop appropriate category and criteria weighting. This part of the decision making process is too important to leave it to single groups with certain political interest. Broad societal involvement and discussion is needed to successfully finish the decision making process and to select the "right" biomass conversion systems within an emerging bio-economy. Energy and resource security is crucial for future economic growth and stable/increasing human living standards. Future research has therefore to be undertaken accurately and diligently for a successful transformation our oil-based economy to the desired bio-economy.

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ANNEX

A. Extension of the test data set (Section 2.3)

For the example from Section 2.3, it is assumed that over time there will be an additional (a fourth) biomass conversion system worth to be assessed in the same manner as the above. Table A additionally shows the corresponding data set for a 'biomass conversion system 4' which can be incorporated into the assessment. As MCBB is a MCDM method, its results are strictly dependent on the best values for each criterion provided by the assessed processes itself. The introduction of a new data set consequently can lead to a shift of these benchmarks previously used to newly introduced criteria values by an extended criteria value matrix C.

Table A: Random test data and calculations for the demonstration of the MCBB approach.

Biomass conversion system No.	**Criterion No.**						
	1	**2**	**3**	**4**	**5**	**6**	**7**
C : Criteria value matrix (extended random test data)							
1	0.045	8	90.0	25.0	20.0	0.03	4.000
2	0.06	4	100.0	10.0	18.0	0.04	2.500
3	0.02	5	75.0	45.0	30.0	0.025	1.200
4	0.1	6	45.0	15.0	31.0	0.05	3.600

Utilizing the presented example, the reapplication of Eq. 2.1 and 2.11 to a new matrix C delivers the following two vectors V^{max} and V^{min} (the changes have been highlighted in bolt):

(1) $$V^{max} = (\mathbf{0.1}; 8; 100; 45; \mathbf{31}; \mathbf{0.05}; 4000)$$

(2) $$V^{min} = (0.02; 4; \mathbf{45}; 10; 18; 0.025; 1200)$$

The changes within V^{min} and V^{max} lead to a change of results in the normalization process using Eq.2.13 and further to a change of the decision vectors in Eq. 2.33:

(3) $$B^{u} = \begin{pmatrix} 53{,}0\% \\ 49{,}1\% \\ 39{,}7\% \\ 50{,}0\% \end{pmatrix} \begin{matrix} Biomass\ conversion\ system\ 1 \\ Biomass\ conversion\ system\ 2 \\ Biomass\ conversion\ system\ 3 \\ Biomass\ conversion\ system\ 4 \end{matrix}$$

(4) $$B^{w} = \begin{pmatrix} 52{,}4\% \\ 54{,}5\% \\ 38{,}3\% \\ 57{,}9\% \end{pmatrix} \begin{matrix} Biomass\ conversion\ system\ 1 \\ Biomass\ conversion\ system\ 2 \\ Biomass\ conversion\ system\ 3 \\ Biomass\ conversion\ system\ 4 \end{matrix}$$

Due to the introduction of the criteria values of 'Biomass conversion system 4', 'Biomass conversion system 1' loses its dominance against 'Biomass conversion system 2' due to the extension of the benchmarking range or bandwidth inside the calculation process. 'Biomass conversion system 4' becomes the dominant process technology from the assessment now. This behavior of MCBB shows its dynamic property and gives it a flexible feature to cope with flexible framework conditions. Consequently, it is obvious that the ARP illustrations change completely by the introduction of an additional data set. The amendments are shown in Figure A.

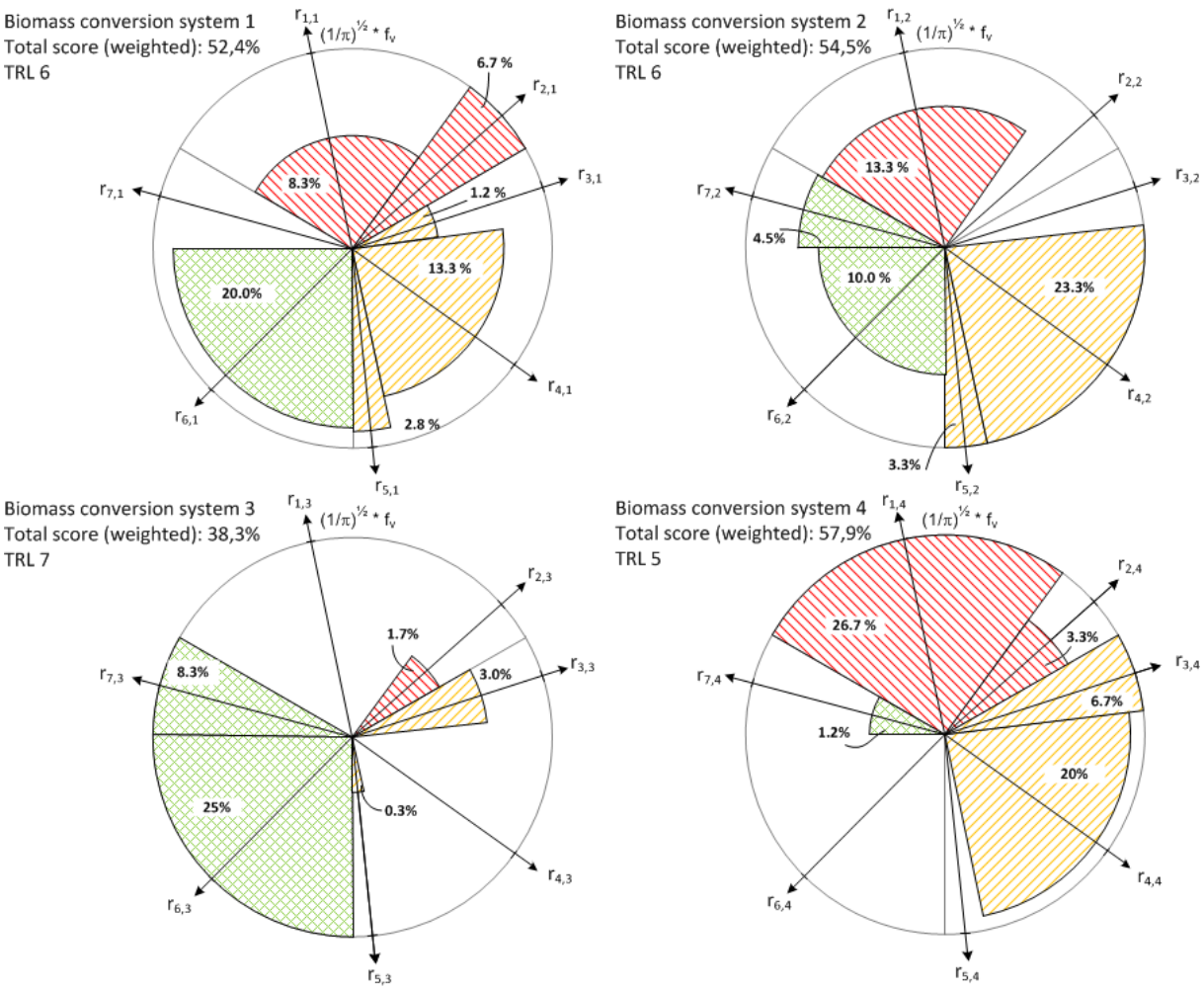

Figure A: Advanced radar plots (ARP) as MCBB result from the extended test data example.

Table B: Experimental raw data for Section 3: Process conditions, input, output, and elemental composition (hydrochar).

Run	Conditions			Input			Output					Elemental composition (hydrochar)					
	Temp.	Catalyst	Time	Digestate	Citronic Acid	Press Water	Hydro-char	Liquids	Gas			C	H	N	S	O	Ash
No. #	T_p (°C)	X (g_{CA}/g_{DM})	d_R (min)	$m_{DG,DM}$ (g)	m_{CA} (g)	m_{pw} (g)	$m_{s,DM}$ (g)	m_ℓ (g)	V_g (ml)	T (°C)	p (mbar)	ξ (wt-%)					
1	245	0.144	140	25.10	3.61	142.24	12.75	155.0	1,340	18.6	974.6	43.9%	4.6%	2.8%	0.5%	13.6%	34.6%
2	220	0.144	320	25.12	3.62	142.37	15.97	152.6	1,130	17.9	966.0	42.9%	4.7%	2.6%	0.5%	18.0%	31.3%
3	220	0.144	320	25.66	3.69	145.38	15.87	158.2	1,330	21.7	971.7	42.4%	4.6%	2.5%	0.4%	19.2%	30.9%
4	220	0.078	140	25.52	1.99	144.62	17.13	153.9	940	15.8	972.3	40.4%	4.7%	2.3%	0.4%	19.4%	32.8%
5	245	0.078	320	25.86	2.01	146.54	13.35	161.6	1,505	17.6	969.6	44.4%	4.6%	3.1%	0.4%	9.6%	37.9%
6	190	0.144	140	26.46	3.81	149.96	19.20	156.5	640	17.6	969.5	41.0%	5.1%	2.2%	0.4%	22.5%	28.8%
7	220	0.078	560	25.70	2.00	145.66	15.23	157.3	1,395	18.4	972.3	43.2%	4.7%	2.7%	0.4%	14.7%	34.3%
8	220	0.144	320	25.63	3.69	145.24	17.07	157.7	1,205	19.5	971.7	42.3%	4.7%	2.6%	0.4%	15.8%	34.2%
9	220	0.548	140	24.05	13.19	136.28	16.74	156.8	2,730	18.8	971.2	45.7%	4.9%	2.1%	0.4%	19.6%	27.3%
10	190	0.548	320	24.07	13.20	136.43	20.51	152.7	2,370	19.2	971.7	46.6%	5.2%	2.1%	1.2%	21.0%	23.9%
11	245	0.144	560	25.67	3.70	145.49	13.40	159.4	1,675	19.2	971.7	45.3%	4.6%	3.2%	0.4%	11.2%	35.3%
12	190	0.144	560	25.59	3.68	145.00	20.08	154.0	890	21.6	968.1	40.4%	4.8%	2.3%	0.5%	20.3%	31.7%
13	190	0.078	320	26.04	2.03	147.58	17.46	158.1	560	21.0	970.2	39.4%	5.0%	2.2%	0.4%	23.3%	29.7%
14	245	0.548	320	24.22	13.28	137.25	15.00	158.0	3,410	19.4	970.9	46.7%	4.8%	2.6%	0.4%	10.7%	34.8%
15	220	0.548	560	23.94	13.13	135.65	16.10	153.1	3,845	20.0	966.4	48.5%	4.9%	2.5%	0.4%	13.0%	30.7%
16	220	0.078	140	25.83	2.01	146.40	17.11	156.2	935	19.0	982.1	42.1%	4.8%	2.3%	0.4%	18.0%	32.4%
17	190	0.144	140	25.66	3.70	145.42	18.67	156.0	685	20.8	965.7	40.0%	5.0%	2.1%	0.4%	25.0%	27.5%
18	245	0.078	320	25.86	2.01	146.56	12.80	162.0	1,615	22.0	968.4	44.8%	4.7%	3.3%	0.6%	8.4%	38.2%
19	190	0.144	560	25.62	3.69	145.19	17.42	157.4	710	20.9	971.9	43.0%	5.0%	2.3%	0.5%	19.1%	30.1%
20	220	0.548	140	24.20	13.27	137.15	16.23	154.4	3,015	20.9	971.9	39.8%	4.3%	1.8%	0.4%	28.5%	25.2%
21	220	0.144	320	25.66	3.69	145.38	16.92	158.2	1,155	24.5	979.7	40.9%	4.6%	2.5%	0.4%	18.6%	32.9%
22	190	0.548	320	24.22	13.28	137.25	18.33	155.1	2,250	24.8	979.4	48.0%	5.4%	2.1%	0.4%	20.3%	23.8%
23	220	0.144	320	25.60	3.69	145.06	17.70	155.0	1,170	22.6	974.7	42.3%	4.8%	2.6%	0.4%	17.4%	32.4%
24	245	0.144	560	25.66	3.69	145.40	15.12	158.3	1,685	19.5	974.0	45.0%	4.7%	3.2%	0.4%	11.2%	35.5%
25	190	0.078	320	25.90	2.02	146.79	16.40	156.7	525	21.6	972.8	40.4%	5.0%	2.3%	0.4%	22.8%	29.0%
26	220	0.548	560	24.20	13.27	137.17	13.96	160.6	3,800	21.8	981.1	50.0%	5.0%	2.5%	0.4%	13.4%	28.7%
27	245	0.144	140	25.65	3.69	145.34	14.30	156.0	1,500	22.1	981.1	45.8%	4.7%	3.5%	0.4%	8.3%	37.2%
28	245	0.548	320	24.22	13.28	137.24	13.91	157.1	3,560	22.8	979.5	47.0%	4.8%	2.6%	0.4%	10.1%	35.2%
29	220	0.078	560	25.88	2.02	146.68	14.39	159.5	1,230	20.9	965.8	43.6%	4.7%	2.9%	0.5%	11.8%	36.5%
30	220	0.144	320	25.63	3.69	145.21	15.95	158.1	1,250	21.3	967.0	42.6%	4.8%	2.6%	0.4%	16.2%	33.4%

Table C: Experimental raw data for Section 3: Gas composition.

Run	Gas composition											
	CO_2	N_2	CO	H_2S	CH_4	H_2	C_3H_6	C_2H_4	C_2H_6	O_2	C_3H_8	Rest[a] (calc.)
No. (#)	ζ (mol-%)											
1	86.20%	3.27%	0.05%	0.18%	0.02%	0.01%	0.03%	0.01%	0.01%	0.98%	-	9.24%
2	87.00%	3.18%	0.24%	0.13%	0.03%	0.03%	-	0.01%	0.01%	0.94%	-	8.43%
3	87.41%	1.25%	0.95%	0.04%	0.08%	0.08%	0.02%	0.02%	0.01%	0.33%	-	9.80%
4	87.82%	2.57%	0.25%	0.16%	0.02%	0.02%	-	0.01%	0.01%	0.76%	-	8.40%
5	87.89%	0.85%	-	0.09%	0.07%	0.04%	0.05%	0.02%	0.02%	0.29%	0.01%	10.67%
6	76.02%	3.84%	0.35%	0.05%	0.02%	0.03%	-	0.01%	-	0.89%	-	18.79%
7	88.67%	0.38%	0.03%	0.15%	0.03%	0.02%	0.01%	0.01%	0.01%	0.11%	-	10.59%
8	89.32%	0.29%	0.22%	0.19%	0.05%	0.05%	0.01%	0.02%	0.01%	0.03%	-	9.81%
9	87.42%	2.76%	0.23%	0.03%	-	-	-	-	-	0.84%	-	8.72%
10	90.11%	0.32%	0.15%	0.03%	0.01%	-	-	-	-	0.09%	-	9.30%
11	88.39%	0.51%	-	0.15%	0.16%	0.09%	0.06%	0.02%	0.03%	0.12%	-	10.49%
12	89.03%	0.37%	0.07%	0.11%	0.01%	0.01%	-	-	-	0.09%	-	10.31%
13	87.22%	2.01%	0.16%	0.04%	0.02%	0.02%	-	0.01%	-	0.56%	-	9.99%
14	88.48%	1.10%	0.55%	0.06%	0.16%	0.15%	0.21%	0.03%	0.03%	0.32%	-	8.92%
15	88.62%	0.75%	1.46%	0.01%	0.08%	0.10%	0.07%	0.02%	0.01%	0.17%	-	8.70%
16	89.97%	0.49%	0.22%	0.23%	0.02%	0.02%	-	0.01%	0.01%	0.11%	-	8.93%
17	86.05%	1.88%	0.44%	0.04%	0.02%	0.02%	-	0.01%	-	0.46%	-	11.08%
18	89.37%	0.17%	-	0.34%	0.07%	0.05%	0.04%	0.02%	0.02%	0.04%	-	9.89%
19	90.99%	0.48%	0.11%	0.07%	0.02%	0.01%	-	-	-	0.12%	-	8.20%
20	87.49%	1.08%	1.83%	0.01%	0.04%	0.03%	0.01%	0.01%	-	0.31%	-	9.19%
21	85.03%	1.32%	0.85%	0.05%	0.08%	0.09%	0.03%	0.02%	0.02%	0.28%	-	12.24%
22	86.31%	1.16%	0.17%	-	-	-	-	-	-	0.40%	-	11.97%
23	88.71%	0.90%	0.73%	0.14%	0.09%	0.07%	0.03%	0.02%	0.01%	0.15%	-	9.15%
24	88.99%	0.87%	0.36%	0.12%	0.29%	0.20%	0.11%	0.04%	0.06%	0.15%	-	8.81%
25	87.43%	1.32%	0.23%	0.03%	0.02%	0.02%	-	0.01%	-	0.30%	-	10.65%
26	89.91%	0.34%	0.03%	0.05%	-	-	0.03%	-	-	0.11%	-	9.53%
27	87.57%	1.19%	1.25%	0.08%	0.18%	0.24%	0.09%	0.05%	0.04%	0.14%	-	9.17%
28	87.47%	1.15%	0.63%	0.05%	0.15%	0.15%	0.20%	0.03%	0.03%	0.29%	-	9.86%
29	89.50%	0.47%	0.07%	0.15%	0.02%	0.02%	-	0.01%	0.01%	0.12%	-	9.64%
30	88.36%	0.30%	0.14%	0.26%	0.03%	0.03%	0.01%	0.01%	0.01%	0.08%	-	10.76%

[a] Almost Argon (Ar).

Table D: Experimental raw data for Section 3: Process water content.

Run	Process water content											
	Formic acid	Acetic Acid	Glycine	Formal-dehyde	Acetal-dehyde	NH_4	Cl	PO_4	SO_4	DOC	TNb	Phenol -Index
No. (#)	(mg/l)											
1	723.9	3,816.5	2,012.9	<10	179.2	1,754	1,665.0	140.8	355.2	17,222	3,777	546
2	1,342.1	3,675.2	1,679.8	<10	152.8	1,861	1,781.3	231.2	283.7	19,791	4,238	527
3	1,022.3	2,977.4	1,418.4	<10	<10	1,658	1,766.9	174.5	262.7	17,385	3,825	422
4	1,608.7	2,874.6	1,340.2	916.6	<10	1,768	1,553.5	103.3	364.0	17,689	4,158	413
5	266.3	3,179.4	1,745.9	898.4	179.5	1,765	1,625.7	249.4	478.9	13,846	3,622	442
6	1,798.0	3,013.6	960.9	739.3	258.4	1,606	1,991.1	1,091.7	570.2	23,351	4,685	358
7	1,086.2	3,014.0	1,650.1	866.6	148.9	1,752	1,756.1	123.4	350.4	15,703	3,781	428
8	745.8	2,099.4	1,105.4	642.7	<10	1,253	1,300.3	90.6	91.6	11,557	2,762	288
9	2,168.4	4,280.9	3,406.9	1,581.3	918.3	767	1,229.8	1,071.8	672.7	25,904	3,360	150
10	2,900.1	3,990.9	3,192.6	3,933.7	2,410.7	1,005	1,713.5	1,568.7	871.0	33,305	4,372	325
11	218.2	4,160.5	2,146.7	n.f.	232.0	2,230	2,099.6	367.0	495.5	14,889	3,544	506
12	1,913.0	3,355.0	1,624.0	928.4	n.f.	2,081	2,114.6	212.5	150.0	22,185	4,764	390
13	1,986.6	3,671.1	1,160.2	623.4	n.f.	1,754	1,780.7	84.7	315.3	17,951	3,925	333
14	342.8	5,374.9	3,379.0	n.f.	322.0	2,189	1,986.0	59.5	614.8	22,216	3,910	497
15	1,765.0	6,267.1	4,913.0	n.f.	573.6	1,780	1,989.6	866.1	267.7	28,022	4,244	467
16	1,581.8	3,098.6	1,498.5	774.6	n.f.	1,801	1,626.9	191.6	509.3	16,070	4,046	454
17	1,671.6	2,591.5	872.3	700.7	249.4	1,555	2,034.9	443.8	301.0	20,423	3,844	359
18	232.8	6,014.3	1,995.1	696.2	164.0	2,045	2,138.2	110.8	237.6	14,317	3,578	494
19	1,741.0	2,956.6	1,550.4	888.6	n.f.	1,463	1,914.9	141.4	232.2	18,479	3,745	383
20	3,166.3	5,621.6	4,744.1	2,327.2	1,314.6	1,164	2,030.4	1,520.5	717.1	35,059	4,719	488
21	1,334.7	3,398.7	1,576.6	1,465.6	n.f.	2,350	2,268.3	121.1	366.5	21,114	4,269	354
22	2,128.2	2,792.3	3,087.0	3,021.3	250.1	1,150	1,546.9	3,016.1	1,326.0	39,220	4,726	329
23	1,291.0	4,522.2	2,116.4	1,088.3	n.f.	2,300	1,993.8	124.4	214.9	18,902	4,062	401
24	248.7	5,804.8	2,389.3	1,226.7	166.5	3,380	2,381.0	315.7	240.9	19,445	4,341	401
25	1,732.2	5,121.2	835.2	450.2	n.f.	1,860	1,747.5	189.8	267.2	18,081	3,621	330
26	658.0	2,963.9	2,393.2	1,882.3	113.7	1,380	1,485.2	688.2	305.1	24,672	3,095	450
27	576.1	3,781.4	2,008.0	1,245.1	131.9	2,160	1,883.5	181.6	278.8	18,018	3,473	547
28	574.5	5,313.1	2,723.1	2,950.3	421.1	2,540	1,847.4	256.0	183.9	25,381	3,992	523
29	653.1	5,195.1	801.5	348.9	n.f.	2,330	1,726.3	197.0	275.7	15,315	3,400	435
30	1,226.0	3,558.5	1,355.4	423.7	n.f.	2,190	1,887.3	106.6	283.2	15,751	3,598	398

n.f. = not found, DOC = dissolved organic carbon, TNb = total nitrogen bound

Table E: Experimental raw data for Section 4: Process conditions, input, output, and elemental composition (hydrochar).

Run	Conditions			Input			Output					Elemental composition (hydrochar)					
	Temp.	Catalyst	Time	Digestate	Citronic Acid	Press Water	Hydro-char	Liquids	Gas			C	H	N	S	O	Ash
No. #	T_p (°C)	X (mg_{CA}/g_{DM})	d_R (min)	$m_{DG,DM}$ (g)	m_{CA} (mg)	m_{pw} (g)	$m_{s,DM}$ (g)	m_ℓ (g)	V_g (ml)	T (°C)	p (mbar)	ξ (wt-%)					
1	190	20.0	330	22.81	467.00	129.21	16.33	134.8	565	20.8	972.4	51.6%	5.9%	1.0%	0.1%	36.8%	4.6%
2	190	20.0	330	22.83	467.00	129.37	15.86	134.6	220	18.9	975.4	52.4%	5.9%	1.0%	0.1%	37.2%	3.4%
3	245	20.0	330	22.83	466.00	129.35	9.76	138.1	1,990	24.2	975.5	66.7%	5.3%	1.4%	0.1%	19.8%	6.7%
4	245	20.1	330	22.80	467.00	129.17	10.24	136.8	1,790	18.9	975.4	67.7%	5.5%	1.4%	0.1%	19.0%	6.3%
5	190	0.0	330	22.80	0.00	129.47	19.34	128.4	355	10.9	979.2	53.6%	5.4%	0.8%	0.6%	36.1%	4.1%
6	190	0.0	330	22.88	0.00	129.66	18.55	133.4	520	19.3	967.2	52.8%	5.9%	1.0%	0.1%	33.2%	7.0%
7	245	0.0	330	22.84	0.00	129.52	10.23	136.6	1,400	14.2	982.7	70.5%	5.3%	1.5%	0.1%	15.4%	7.3%
8	245	0.0	330	22.87	0.00	129.58	9.57	140.0	1,605	21.2	973.0	68.6%	5.8%	1.4%	0.1%	15.1%	9.1%
9	190	1.8	150	22.79	40.00	129.08	18.91	131.6	405	26.3	974.4	50.2%	6.2%	0.7%	0.1%	38.6%	4.2%
10	190	1.7	150	22.81	38.00	129.21	16.84	135.2	295	22.6	970.9	51.2%	6.0%	1.0%	0.1%	34.9%	6.8%
11	245	1.7	150	22.87	40.00	129.23	10.21	138.6	1,435	18.8	982.2	66.6%	5.6%	1.3%	0.2%	19.9%	6.4%
12	245	1.7	150	22.81	38.00	129.23	12.22	134.8	1,570	21.9	977.7	66.3%	5.7%	1.4%	0.1%	19.6%	6.9%
13	190	1.7	570	22.83	40.00	129.47	18.82	132.5	590	16.9	968.9	52.7%	6.0%	0.8%	0.1%	35.9%	4.5%
14	190	1.7	570	22.91	38.00	129.80	17.53	133.3	375	22.6	970.9	52.4%	5.9%	1.0%	0.1%	36.3%	4.3%
15	245	1.7	570	22.79	39.00	129.23	10.84	136.5	1,665	23.0	966.9	67.7%	5.7%	1.4%	0.1%	17.2%	7.8%
16	245	1.7	570	22.80	38.00	129.17	10.22	137.1	1,635	18.2	975.3	67.6%	5.6%	1.5%	0.1%	18.7%	6.5%
17	220	20.0	150	22.81	466.00	129.20	14.59	136.5	955	18.1	969.1	56.2%	5.8%	1.0%	0.1%	29.9%	7.0%
18	220	20.1	150	22.82	467.00	129.31	15.60	135.9	925	20.0	975.3	55.8%	5.9%	1.0%	0.1%	30.6%	6.6%
19	220	0.0	150	22.86	0.00	129.44	15.83	133.9	325	11.0	979.2	57.6%	5.6%	1.0%	0.1%	30.7%	5.1%
20	220	0.0	150	22.87	0.00	129.58	15.62	133.8	855	19.1	967.8	54.8%	5.9%	1.0%	0.1%	31.5%	6.8%
21	220	20.1	570	22.82	467.00	129.25	12.76	135.4	1,070	16.7	969.1	64.9%	5.8%	1.2%	0.1%	22.4%	5.6%
22	220	20.1	570	22.81	468.00	129.33	13.37	134.8	955	24.8	979.5	64.8%	5.7%	1.3%	0.1%	20.2%	8.0%
23	220	0.0	570	22.83	0.00	129.42	12.94	134.9	1,255	12.0	983.6	66.8%	5.3%	1.3%	0.1%	20.4%	6.2%
24	220	0.0	570	22.87	0.00	129.57	12.05	136.5	1,435	21.5	977.2	64.4%	5.7%	1.3%	0.1%	20.3%	8.3%
25	220	1.8	330	22.80	40.00	129.28	13.97	134.1	1,140	17.5	968.3	60.6%	5.8%	1.1%	0.2%	26.8%	5.5%
26	220	1.7	330	22.79	39.00	129.17	13.13	135.8	1,270	19.3	967.2	60.2%	5.8%	1.1%	0.1%	25.7%	7.1%
27	220	1.7	330	22.86	39.00	129.49	12.52	137.0	705	18.8	971.6	60.7%	5.8%	1.1%	0.2%	27.0%	5.2%
28	220	1.7	330	22.80	38.00	129.17	13.18	135.4	1,070	22.0	974.2	59.7%	5.7%	1.2%	0.1%	28.2%	5.1%
29	220	1.8	330	22.72	40.00	128.69	14.21	134.3	1,235	20.6	969.3	60.7%	5.8%	1.1%	0.1%	27.3%	5.0%
30	220	1.7	330	22.87	39.00	129.57	14.16	135.8	1,265	22.6	970.9	59.9%	5.8%	1.1%	0.1%	25.6%	7.5%

Table F: Experimental raw data for Section 4: Gas composition.

Run	Gas composition											
	CO_2	N_2	CO	H_2S	CH_4	H_2	C_3H_6	C_2H_4	C_2H_6	O_2	C_3H_8	Rest[a] (calc.)
No. (#)	ζ (mol-%)											
1	85.70%	1.85%	1.24%	-	0.01%	0.01%	-	-	0.01%	-	-	11.16%
2	74.92%	2.75%	1.46%	-	0.02%	0.02%	-	-	0.01%	-	-	20.83%
3	88.34%	0.38%	0.39%	0.01%	0.04%	0.07%	-	0.01%	0.01%	-	-	10.74%
4	82.63%	1.51%	5.00%	-	0.23%	0.51%	-	0.05%	0.04%	-	-	10.05%
5	87.40%	2.82%	1.41%	-	0.02%	0.02%	-	-	0.01%	-	-	8.32%
6	83.70%	2.35%	1.47%	-	0.02%	0.02%	-	-	0.01%	-	-	12.43%
7	89.20%	1.51%	0.45%	-	0.05%	0.09%	-	0.01%	0.01%	-	-	8.68%
8	87.32%	1.81%	0.33%	-	0.07%	0.05%	-	0.01%	0.01%	-	-	10.41%
9	75.28%	3.89%	1.46%	-	0.03%	0.02%	-	-	0.01%	-	-	19.31%
10	77.22%	3.50%	1.59%	-	0.02%	0.02%	-	-	0.01%	-	-	17.64%
11	89.17%	0.43%	1.21%	-	0.03%	0.09%	-	0.01%	0.01%	-	-	9.05%
12	89.56%	0.68%	0.58%	-	0.02%	0.03%	-	-	0.01%	-	-	9.11%
13	87.80%	1.33%	1.07%	-	0.01%	0.01%	-	-	0.01%	-	-	9.77%
14	87.04%	1.32%	1.97%	-	0.02%	0.03%	-	-	0.01%	-	-	9.61%
15	88.78%	0.65%	0.09%	-	0.02%	0.02%	-	0.01%	0.01%	-	-	10.42%
16	90.35%	0.45%	0.10%	-	0.02%	0.02%	-	0.01%	0.01%	-	-	9.05%
17	87.47%	1.06%	1.61%	-	0.02%	0.03%	-	-	0.01%	-	-	9.81%
18	88.42%	0.73%	1.48%	-	0.01%	0.03%	-	-	0.01%	-	-	9.32%
19	82.77%	1.81%	4.04%	-	0.05%	0.11%	-	0.01%	0.02%	-	-	11.20%
20	85.94%	1.41%	2.07%	-	0.02%	0.05%	-	-	0.01%	-	-	10.50%
21	89.05%	1.14%	0.38%	-	0.01%	0.01%	-	-	0.01%	-	-	9.41%
22	88.59%	0.79%	1.13%	-	0.02%	0.04%	-	-	0.01%	-	-	9.42%
23	72.31%	4.34%	0.49%	-	0.56%	0.02%	-	-	0.01%	-	-	22.28%
24	88.82%	1.40%	0.53%	-	0.01%	0.02%	-	-	0.01%	-	-	9.22%
25	87.68%	0.97%	1.36%	-	0.02%	0.05%	-	-	0.01%	-	-	9.92%
26	84.91%	0.89%	3.61%	-	0.05%	0.12%	-	0.01%	0.01%	-	-	10.40%
27	87.59%	0.66%	1.19%	-	0.02%	0.04%	-	-	0.01%	-	-	10.49%
28	92.43%	0.35%	1.24%	-	0.02%	0.04%	-	-	0.01%	-	-	5.91%
29	87.89%	0.75%	1.23%	-	0.03%	0.04%	-	-	0.01%	-	-	10.05%
30	88.78%	0.56%	0.72%	-	0.01%	0.02%	-	-	0.01%	-	-	9.90%

[a] Almost Argon (Ar).

Table G: Experimental raw data for Section 4: Process water content.

Run	Process water content								
	Formic acid	Acetic Acid	Glycine	Cl	PO_4	SO_4	DOC	TNb	HMF
No. (#)	(mg/l)								
1	1,002	5,971	1,165	576	452	463	12,861	588	521
2	2,214	6,314	1,027	521	356	435	19,831	498	893
3	344	7,900	3,005	503	192	363	17,802	410	n.f.
4	147	7,504	3,299	547	201	465	13,936	420	n.f.
5	1,537	5,347	1,282	542	389	633	12,534	551	444
6	1,943	5,716	1,316	519	382	639	9,776	450	371
7	442	8,623	3,490	565	158	500	15,181	405	n.f.
8	167	7,590	3,447	540	156	478	14,097	401	n.f.
9	1,682	5,198	1,255	590	536	754	14,012	619	643
10	2,002	4,580	1,015	425	329	511	12,895	492	579
11	485	8,354	3,029	547	237	502	15,887	429	n.f.
12	568	7,474	3,322	628	305	638	9,570	487	2
13	1,244	5,448	1,270	554	429	674	8,746	523	244
14	1,286	5,086	1,296	578	433	726	10,701	546	278
15	321	9,198	3,577	594	182	514	10,606	388	n.f.
16	999	7,615	3,469	538	166	464	13,816	407	n.f.
17	1,534	5,518	1,613	504	366	741	9,685	460	241
18	1,743	6,000	1,682	550	219	359	13,529	538	319
19	1,267	5,913	2,023	589	138	446	8,879	544	164
20	1,348	5,787	1,894	608	148	408	12,597	547	269
21	698	6,589	2,009	548	426	678	13,000	434	29
22	609	6,851	2,325	549	244	508	12,801	440	29
23	585	6,772	2,607	566	224	679	10,794	442	24
24	706	6,376	2,247	575	227	686	13,485	418	34
25	774	6,419	2,078	551	211	663	16,214	551	130
26	972	6,127	2,134	561	217	721	5,621	443	136
27	731	6,175	2,129	571	214	718	13,248	450	118
28	891	6,143	2,157	514	166	633	16,466	452	128
29	972	6,246	2,119	535	262	706	15,961	444	115
30	1,471	6,315	2,135	557	189	705	16,639	458	132

n.f .= not found, DOC = dissolved organic carbon, TNb = total nitrogen bound

C. Curriculum Vitae

Personal Data

Name:	Kay Suwelack (birth name Katzmarek)
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Marital status:	Married, three children
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Professional Experience

01/2013-present	Fraunhofer Institute for Technological Trend Analysis INT, Euskirchen, Germany	
	05/2015-present	Deputy Head of Business Unit
	01/2013-04/2015	Research Fellow
05/2011-12/2012	PricewaterhouseCoopers, Düsseldorf, Germany	
	11/2011-12/2012	Authorized Officer (Prokurist)
	05/2011-12/2012	Manager (Managing Consultant)
10/2008-04/2011	KEMA (today DNV GL), Bonn, Germany	
	01/2011-04/2011	Senior Consultant
	10/2008-12/2010	Consultant
11/2006-09/2008	agri.capital (today AC Biogas), Münster, Germany	
	02/2007-09/2008	In-house Consultant | Assistant to the Technical Director (CTO)
	11/2006-01/2007	Project Controller
08/2005-09/2005	E.ON Kernkraft, Schweinfurt, Germany	
	Intern | Hot-Zone-Control Department | Nuclear Power Plant Grafenrheinfeld	
10/2001-12/2001	AHK Saudi Arabia, Riyadh, Saudi Arabia	
	Intern | Marketing Department | German Foreign Trade Chamber	
08/1996-09/1997	Alexianer Hospital, Münster, Germany	
	Social Service (in lieu of Military Service)	

Education

07/2013-09/2016	Hohenheim University, Institute of Agricultural Engineering, Chair of Conversion Technology and Life Cycle Assessment of Renewable Resources, Stuttgart, Germany Graduation: PhD in Agricultural Science (Dr. sc. agr.)
05/2006-08/2006	Karlsruhe Institute of Technology (KIT), Institute of Technical Chemistry (today Institute of Catalysis Research and Technology), Karlsruhe, Germany Diploma Thesis | Environmental Engineering
10/2004-10/2006	Dresden University of Technology, Dresden, Germany Student | Environmental Engineering Graduation: Diplom-Umwelttechniker (Dipl.-Uwt.)
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